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ROOM TEMPERATURE CURING EPOXY RESIN COMPOSITIONS HIGH TEMPERATU--ETC(U)

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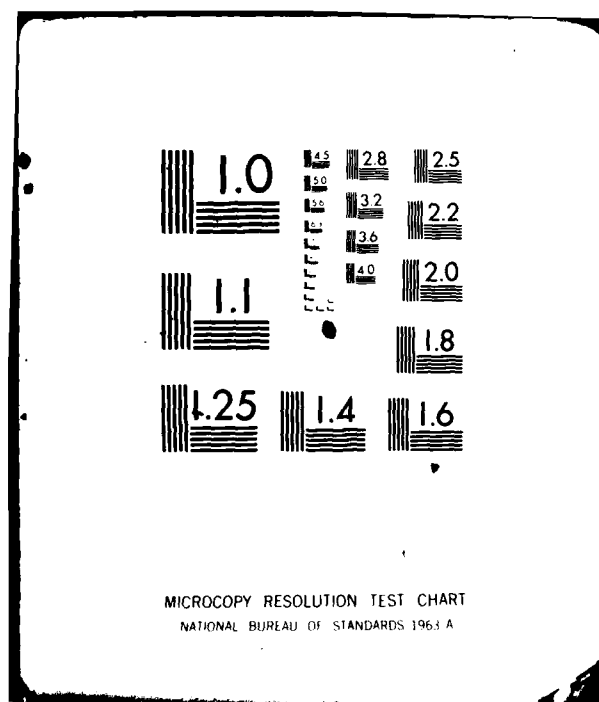
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FINAL REPORT

ROOM TEMPERATURE CURING EPOXY RESIN COMPOSITIONS
HIGH TEMPERATURE SERVICE CAPABILITY FOR FIBER
REINFORCED STRUCTURES, ADHESIVES AND SEALANTS

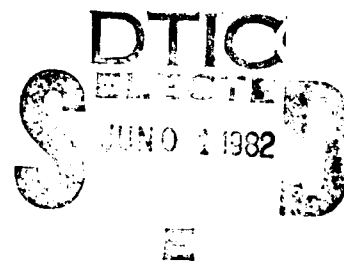
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Room temperature curing epoxy resin compositions with high temperature service capability based on selected high functionality epoxy polymers and multicomponent curing agent systems were formulated and evaluated as binders for glass fiber reinforced laminates, adhesives and sealants. Experimental data have been developed which show that certain suitably formulated two-component epoxy resin compositions can be employed to prepare glass fiber reinforced composites for service up to 200 C. Their high temperature perfor-		

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ABSTRACT (Cont'd)

mance capability significantly exceeds that of other commercially available room temperature curing systems such as polyesters and acrylics. Data are also presented on similarly formulated adhesive compositions which show promise for usage over an exceptionally wide temperature range.

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ROOM TEMPERATURE CURING EPOXY RESIN COMPOSITIONS
HIGH TEMPERATURE SERVICE CAPABILITY FOR FIBER REINFORCED
STRUCTURES, ADHESIVES AND SEALANTS

SUMMARY

The increasing demand for nonmetallic materials with high temperature service capability in aerospace and industrial applications is being met both by the development of new resins and improvements in compounding/processing technology. Resin compositions with high temperature service capability which can be cured at ambient temperatures, are of particular interest for the manufacture of fiber reinforced composites for reasons ranging from energy savings in processing to simplified field repair of damaged composite structures. They offer potentially equally impressive advantages for adhesive and sealant usage. Room temperature curing two component resin systems based on selected high functionality epoxy polymers and multicomponent curing agent compositions were formulated and evaluated as matrices for glass fiber reinforced laminates and also as adhesives and sealants. Experimental data are presented which show that certain suitably formulated epoxy resin compositions can be used to prepare glass fiber reinforced composites for prolonged service up to 200 C. Exploratory tests of the performance of these room temperature curing epoxy systems at elevated temperatures up to 200 C are also reported. The high temperature performance of such laminates and adhesives significantly exceeds that of other room temperature curing polymer

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systems such as polyesters and acrylics. Adhesives formulated with these room temperature curing high functionality epoxy resin compositions offer considerable promise for use over the exceptionally wide temperature range of -50 C to +200 C. Even without state-of-the-art compounding their performance compares favorably with that of various commercially available room temperature curing adhesive compounds.

I. INTRODUCTION

There has in recent years been an increasing demand for fiber reinforced composite materials, adhesives and sealants having utility at high temperature service conditions both for aerospace and industrial applications. The continuing development of high temperature resistant polymers and steady improvements in compounding/processing technology are beginning to meet a great many current performance requirements. Recently the possibility of employing room temperature curing resins with high temperature service characteristics has aroused considerable interest for the more cost effective manufacture especially of fiber reinforced composite structures. Such room temperature curing resin systems could lower manufacturing costs of the composites by virtue of sharply reduced energy usage in processing and thus enhance the competitive position of high performance composites vis a vis other construction materials. They could likewise simplify currently used repair procedures especially under field conditions. This in turn would enlarge the possible applications for high performance composites which must be used at elevated temperatures.

Epoxy resins with their high physical strength properties, toughness, corrosion resistance, excellent electrical insulating properties and ready processability etc., have emerged as the most important matrix materials for high performance fiber reinforced structures. They have likewise gained a predominant position in adhesive and sealant compositions. Perhaps the most outstanding characteristic of epoxy resins is their versatility.¹⁾²⁾ Depending upon the physical and chemical nature of the epoxy resin, the type and amount of the curing agent, fillers and other additives used as well as the curing

conditions employed, it is possible to obtain cured materials with a wide range of highly reproducible, 'tailor made' processing and performance properties. Epoxy resins are therefore extensively employed not only for the manufacture of fiber reinforced composites but also for adhesives, sealants, coatings, potting and encapsulating compounds and so on, generally for use up to 250 - 300 F.

Higher temperature resistance of epoxy resins can be achieved by virtue of the proper selection of both the resin and the curing agent as well as judicious choice of reinforcements, fillers and other additives plus optimization of processing conditions. An extensive body of research and development work indicates that temperature resistance and frequently chemical resistance can be achieved by increasing the functionality of either the epoxy resin or the curing agents. This results in higher cross-link densities of the cured resins and hence, improved thermal stability. Other variables which can affect the temperature resistance of the epoxy resins range from the use of thermally stable reinforcements, fillers, etc., to carefully controlled curing schedules. Today epoxy resin compositions can be formulated which can be used for prolonged time periods up to 200 C in the form of fiber reinforced composites, adhesives, sealants and coatings.

The preparation of room temperature curing epoxy resin compositions with high temperature service capability is being attempted by a number of approaches involving mainly specific types of polyfunctional epoxies and various selected modified highly functional curing agents including aromatic dianhydrides. The preferred curing agents have been based on organic acid dianhydrides which contain other cyclic or aromatic structures including pyromellitic dianhydride

(PMDA), benzophenone tetracarboxylic dianhydride (BTDA), also cyclopentadiene dianhydride. These materials while effective in upgrading this heat resistance of epoxy resin compounds, are difficult to use because of their high melting points, very limited solubility in either the epoxy resin or a common solvent and lack of reactivity with epoxy resins at ambient temperatures. One recent patent claims that such high melting point dianhydrides are solubilized at room temperature in the presence of polyglycidyl derivatives of aminophenols to give cured epoxy resin systems characterized by high temperature resistance and also enhanced resistance to corrosive chemicals.³⁾ A preferred polyglycidyl derivative is triglycidyl para-aminophenol sold commercially by Ciba Geigy Corporation under the designation Epoxy Resin 0500⁴⁾.

This report describes a program of experimental research on an alternative approach for high temperature resistant epoxy resin development with room temperature curing capability carried out at New York University's Department of Applied Science for the Naval Air Systems Command (Washington,D.C.) . It comprises the formulation of two-component room temperature curing epoxy resin compositions from multifunctional epoxy resins and multicomponent hardener mixtures, a key ingredient of which is an imidazole type curing agent. Data are presented on the experimental evaluation of such room temperature curing two component epoxy resin compositions for the preparation and evaluation of glass fiber reinforced composites, adhesives, etc., for prolonged service up to temperature in the order of 200 C. The high temperature performance of these epoxy resin compositions is also compared with that of other room temperature curing polymer systems such as polyesters and acrylics.

II. EXPERIMENTAL

A program of experimental investigations has been carried out for the Naval Air Systems Command to develop room temperature curing polymer systems with high temperature service capability for use in fiber reinforced structures, adhesives and sealants. This report describes the investigations relating to the development of room temperature curing epoxy component resin systems with high temperature service capability for these applications. The experimental studies comprised the formulation, processing and evaluation of such epoxy resin systems as matrices for glass fiber cloth reinforced composites and also adhesives, primarily in terms of reproducible physical strength properties at both ambient or elevated temperatures.

Extensive screening of commercially available epoxy resins and curing agents resulted in the development of two component room temperature curing epoxy resin systems which were experimentally shown to exhibit remarkably high service temperature capabilities. The basic approach employed for preparing these formulations of two-component room temperature curing epoxy resin systems has been found to have considerable compounding latitude. In its most general form it comprises high functionality epoxy resins and multicomponent hardeners selected to require minimum chain extension and cross linking reactions to attain the molecular weights and degree of cross linking required for use as matrix resins for high performance composites and in adhesives.

More specifically these two-component room temperature curing epoxy resins are composed of high functionality epoxy resins either as such or in blends with a conventional bisphenol A type epoxy (component A) and multicomponent hardeners an important ingredient of which may be an imidazole type compound (type B). Table 1 summarizes the basic properties of three different high functionality epoxy resins namely, MY720, Epoxy Resin 0500 and EPN 1138

which were employed either per se or together with a conventional bisphenol A type epoxy resin for the formulation of room temperature curing epoxy resin systems with high temperature service capability. Blends of MY720, EPN 1138 or Epoxy Resin 0500 with a conventional bisphenol A type of epoxy resin are preferred as they were found to be easier processable and lower in cost while still providing the desired improved high temperature service capability achieved with the high functionality epoxy resins alone. Other types of high functionality epoxy resins including the ECN's, etc., may of course be used as well.

The curing agents for these different epoxy resins and/or resin blends may be comprised of two or three components, e.g., a) a room temperature curing polyfunctional aliphatic polyamine; b) a long chain high molecular weight polyamide, and c) an imidazole compound such as 2 ethyl, 4 methyl imidazole; 2 methyl imidazole or the like. The aliphatic polyamine was triethylene tetramine and the polyamide General Mills Versamid 840 (see Table 2). A substantial amount of experimental work has confirmed that the presence of the imidazole component in the curing agent can markedly enhance the high temperature strength and thus the service capability of such epoxy resin compositions while products such as the aliphatic polyamide can contribute to toughness. Also alternatively flexible epoxy resins could be used in component A in place of say the polyamide (component B) to obtain greater toughness.

A typical generalized formulation for such a two-component room temperature curing epoxy resin with high temperature service capability is shown in Table 2. The room temperature pot life of such a formulation can vary anywhere from 2-4 hours varying inversely with the amount of the aliphatic polyamine as well as volume of material mixed and also temperature.

A satisfactory room temperature can be generally obtained within 24-48 hours. The optimal elevated temperature strength

TABLE 1: TYPICAL PROPERTIES OF SELECTED POLYFUNCTIONAL EPOXY RESINS*

RESIN DESIGNATION	MY720	EPOXY RESIN 0500	EPN 1138	EPON 828
Appearance	clear dark brown semi-solid	clear brown liquid	clear brown semi-solid	clear amber liquid
Viscosity at 25 C (77 F), cps	20,000	3000	20,000-50,000	10-12,000
Viscosity at 52 C (125F), cps, av.	0.80	0.90	0.56	-
Epoxy content, eq/100 g	1.22	10.2	10.2	9.7
Weight per gallon at 25 C (77 F)	1.22	1.22	1.22	-
Specific gravity, 25 C/4 C (77 F/39 F)	100	100	100	100
Solids content, %	4.0	3.0	3.6	2.0
Functionality				

* Ciba Geigy Corporation, Ardsley, New York

TABLE 2: TYPICAL ROOM TEMPERATURE CURING HIGH TEMPERATURE RESISTANT EPOXY FORMULATION

COMPONENT	(TWO COMPONENT TYPE)	PARTS BY WEIGHT
Component A: Resin		
Multifunctional epoxy resin		100-60
bifunctional epoxy resin		0-40
Component B: Curing Agent		
aliphatic polyamine (TETA)		7-15
aliphatic polyamide (Versamid 840)		90-83
Imidazole type compound (2-ethyl 4 methyl imidazole)		3-5
Mix ratio		100A/ 70B-100A/ 50B

properties are realized upon heating which is believed to activate the imidazole component of the curing agent compositions.

Glass fiber cloth laminates were prepared by impregnating 12 plies of 181 style Volan A treated fiberglass cloth with selected two-component room temperature curing epoxy resins systems formulated for high temperature service capability. The wet lay-ups were cured at ambient temperatures and pressures in the order of 15 psi. Physical strength properties were evaluated in accordance with the accepted MIL test procedures after the initial 48 hour cure period and, following that time, exposure of the cured epoxy laminate to elevated temperatures up to 200 C (394 F) for time periods up to 28 days. Resistance to water was ascertained after both water immersion of the room temperature cured epoxy resin laminates at ambient temperatures for specified times and also boiling in water for shorter time periods. The various laminate test results were compared to those obtainable with typical currently used laminates including polyesters and acrylics.

Adhesives were prepared by bonding 2024 aluminum test coupons with specific multifunctional epoxy resin compositions in the lap shear configuration. Lap shear strength measurements were carried out after a 48 hour ambient temperature cure period at both ambient and elevated temperatures up to 200 C (394 F) exposures. All tests were carried out as described in the appropriate MIL test methods, e.g. MMM-A132. The effects of prolonged water immersions, etc., at ambient temperatures on the lap shear bond strengths was also ascertained in this experimental investigation. The test results obtained were evaluated against those realized from various industrially available structural adhesive compositions.

Figures 1, 2 and 3 show the room temperature tensile strengths of three series of 181 style Volan A treated fiberglass cloth reinforced epoxy laminates made respectively with various high functionality epoxy resin blends, namely the MY720/Epon 828, Epoxy Resin 0500/Epon 828 and EPN1138/Epon 828 room temperature curing epoxy resin systems. Test data are presented for multi-component curing agents prepared with and without the 2 ethyl, 4 methyl imidazole component. In figures 4, 5 and 6 there are shown data on the effect of a one week's exposure of 150 C (300 F) on the tensile strengths of the same laminates. Figures 7, 8 and 9 indicate the effect of two week's exposure at 150 C(300 F) on the tensile strengths of these laminates.

These test data show quite clearly that the epoxy resin laminates with the 2 ethyl, 4 methyl imidazole components exhibit both superior tensile strengths and also tensile strength retentions upon 150 C(300 F) exposures. The magnitude of the tensile strengths of the MY720/Epon 828 laminate systems is seen to be significantly higher than that obtained for 100% MY720 laminate system. For the Epoxy 0500/Epon 828 and the EPN1138/Epon 828 laminate systems, however, the tensile strengths are highest for the 100% Epoxy 0500 and 100% EPN 1138 laminate systems. These observations apply to laminates made either with or without the imidazole compound in the curing agent. Flexural strength measurements were also carried out. Figures 10, 11 and 12 show the room temperature flexural strengths of the same series of 181 style Volan A treated fiberglass cloth reinforced laminates made respectively with various high functionality epoxy resin blends namely, the MY720/Epon 828, Epoxy Resin 0500/Epon 828 and the EPN1138/Epon 828 room temperature curing epoxy resin systems. Again, test data are presented for multifunctional curing agents prepared with and without the 2 ethyl, 4 methyl imidazole component. The effects of exposing these different

laminates to 150 C (300 F) for one and two week periods on their flexural strength is depicted in Figures 13 through 18. The data obtained are seen to follow the same trends as the above discussed tensile strength measurements.

Figures 19 to 21 show the effect of prolonged 200 C (394 F) exposures on the tensile strength of room temperature cured laminates made respectively from 80% MY720/20% Epon 828, 80% EPN1138/20%/Epon 828 and 80% Epoxy Resin 0500/Epon 828 epoxy resin blends. Data are presented for laminates made with and without inclusion of the imidazole component in these epoxy resin systems. These test results demonstrate that the inclusion of the 2 ethyl, 4 methyl imidazole component substantially upgrades the 200 C (394 F) performance of these glass fiber cloth reinforced laminates. Similar data for room temperature cured laminates made from analogously formulated epoxy resin compositions containing only 60% of the polyfunctional epoxy resin material in the blends shown in Figures 22 to 24 indicate the same trend .

The resistance of such fiber reinforced laminates to chemicals with special emphasis on water is of considerable interest for many composite applications. One widely used approach for the preliminary evaluation of water resistance comprises boiling of the laminates in water at atmospheric pressure for specified limited time periods. Figures 25, 26 and 27 show the effect of boiling periods up to 8 hours for room temperature cured laminates made from 100% Epoxy Resin 0500, 80% Epoxy Resin 0500/20%/Epon 828 and 100% Epon 828 Resin. The beneficial action of the imidazole -- albeit to a lesser extent -- is again demonstrated. The effects of exposure of these and other laminates to liquid water immersions at ambient temperatures has been determined. Typical test data are summarized in Figure 28. They indicate satisfactory resistance to water immersions at ambient temperature conditions.

Recently there has been expressed considerable interest in the development of "B" stage epoxy prepregs which would be storage stable at ambient temperatures for prolonged time periods without the need for refrigeration. One system which has been proposed for achieving this is comprised of a conventional bisphenol A epoxy resin and 2,5 dimethyl, 2,5 hexane diamine (DMHDA) as the curing agent.⁵⁾

Isophorone diamine and menthane diamine are other curing agents which are proposed to exhibit similar behavior. Preliminary data on the DMHDA epoxy resin system which forms a non-tacky "B" stage after approximately 2 days aging at room temperature, indicates storage stability without refrigeration for time periods exceeding three months. It was deemed of interest to ascertain if the same or a similar curing agent could produce storage stable prepregs with the high functionality epoxy resin blends investigated above. Accordingly, room temperature curing laminates were prepared from typical polyfunctional epoxy resin blends and DMHDA as the curing agent with and without an imidazole additive and tests showed them to produce similarly room temperature stable "B" stage compositions for time periods of at least three months.

Typical test data obtained with 181 style Volan A treated fiberglass cloth reinforced laminates prepared with high functional epoxy resin blends and DMHDA curing agent with and without 2 ethyl, 4 methyl imidazole additive are shown in Figures 29 and 30. Figure 31 shows similar data for laminates made with a typical bisphenol A type epoxy resin, e.g., Epon 828, cured with DMHDA. The test results show that the high temperature tensile strength of the various laminates made with the DMHDA curing agent degrades much more quickly upon 200 C (394 F) exposures than do similar laminates prepared with the previously employed curing agent compositions. Also the water boil tests gave significantly lower results.

Additional experiments were carried out with various isophorone diamine and menthane diamine cured epoxy resin laminates and produced the same type of results.

The 200 C (394 F) and boiling water resistance of fiberglass cloth reinforced laminates prepared with various other room temperature curing matrix resin systems has been compared with that of the previously discussed polyfunctional epoxy resin compositions. Specific alternative room temperature curing laminates were prepared from peroxide cured polyester, vinyl ester and acrylic resin systems. They were Dion GR7000 polyester, Shell Epocryl 480 vinyl ester and AKZO's Diacryl 101 acrylic resins. Figures 32 and 33 show the imidazole containing polyfunctional epoxy resin compositions to exhibit substantially higher thermal stability. Rather surprisingly, the Epocryl 480 vinyl ester resin laminate was found to excell in water resistance as evaluated by a boiling test. The Diacryl 101 resin matrix laminate also had excellent resistance to boiling water.

A considerable amount of work was carried out to explore the applicability of room temperature curing high functionality epoxy resins systems for applications as structural adhesives. At present there are apparently no ambient or even moderately temperature curing epoxy resin compositions which can meet the stringent performance requirements for the manufacture and the repair of high performance composites especially where exposures to elevated temperatures are involved. The highly functional epoxy resin compositions described earlier were therefore experimentally investigated as candidate structural adhesive materials. Lap shear bond strengths of 2024 aluminum alloy coupons were used to screen the adhesive capabilities of these epoxy resin systems. Some experiments were also conducted to ascertain the water resistance of such epoxy adhesive compositions.

Table 3 summarizes the test results obtained from the initial bonding experiments. Lap shear strength data for aluminum test coupons are given at both ambient and elevated temperatures. The aluminum test specimens were prepared for adhesive bonding by the FPL etching procedure. Contact pressure only was applied during cure by tightly wrapping the aluminum coupons in the lap shear configuration with glass fiber tape. All test specimens were permitted to cure at ambient temperatures for a 48 hour time period, prior to testing. The 150 (300 F) test data are reported after a 1/2 hour soak at temperature.

The results obtained are quite encouraging. High functionality epoxy resin blends such as Epoxy Resin 0500/Epon 828, MY720/Epon 828 and EPN 1138/Epon 828 can obviously be formulated with a multicomponent curing agent composition to produce room temperature curing candidate structural adhesives with very definite high temperature use capability. Formulations 1,2,8 and 9 of Table 3 are particularly interesting as regards both the initial and the 150 C (300 F) lap shear strength values obtained. The results are especially noteworthy when it is considered that the maximum flight temperature attained with an advanced aircraft such as the F18 has been experimentally determined to be only around 105 C (210 F).

Tests were also carried out to measure the water absorption characteristics of such room temperature cured high functionality epoxy resin adhesive compositions. These tests involved immersion of the various cured aluminum lap shear test coupons described in Table 3 in deionized water for a 30 day period at ambient temperatures. The weight gain of any of the assemblies tested was less than 2% maximum. Lap shear strengths values of typical high functionality epoxy resin adhesive compositions after this 30 day water immersion period are shown in

Table 4. The results indicate no significant affect for lap shear strength values in Table IV after 30 days water immersion. However, for epoxy resins 8 and 9 the change appears significant.

Another series of experiments were conducted on the effects of various temperature exposures on the short time lap shear strength of three typical room temperature cured high functionality epoxy resin adhesive compositions. The adhesively bonded aluminum lap shear strength assemblies were exposed to temperatures ranging from -50 C(-60 F) to +200 C(394 F). Again all test specimens were permitted to cure at ambient temperatures for a 48 hour time period prior to testing. All temperature tests were carried out after a 1/2 hour soak at the indicated temperature. The test results are summarized in Table 5 below. Data on longer time exposures at elevated temperatures are shown in Figures 34 and 35.

The experimental lap shear strength values presented in Table 5 and Figure 34 and 35 show that such room temperature cured high functionality epoxy resin adhesive compositions feature the remarkably wide service temperature capability from as low as -50 C (-60 F) to as much as +200 C (394 F). This is quite noteworthy especially if it is considered that the specific epoxy resin compositions tested are raw candidate systems and cannot by any means be regarded as finished structural adhesive compounds.

As is well known, the epoxy and other structural adhesives produced commercially today contain various other ingredients which range from special tougheners mainly elastomers, to selected largely inorganic fillers such as for example, aluminum metal powder, to flow control agents, namely, finely divided silicas (cabotsil or equivalent) and adhesion promoters, typically silicone coupling agents. Proper compounding with such additives can be expected to substantially upgrade adhesive

TABLE 3: LAP SHEAR STRENGTHS OF ROOM TEMPERATURE CURING HIGH FUNCTIONALITY EPOXY RESIN SYSTEMS
(2024 ALUMINUM ALLOY COUPONS, FPL ETCH TREATMENT)

	EPOXY RESIN FORMULATION	LAP SHEAR STRENGTH, Psi	
		25 C (77 F)	150 C (300 F)
1.	Epoxy Resin 0500/Epon 828/TETA/840 (60/40/12/40)	2590	1490
2.	Epoxy Resin 0500/Epon 828/TETA/840/2, 4 EMI (60/40/10/40/4)	2670	1640
3.	Epoxy Resin 0500/Epon 828/TETA (60/40/16)	2810	1420
4.	MY720/Epon 828/ TETA/840 (60/40/12/40)	2340	1310
5.	MY720/Epon 828/TETA/840/2, 4, EMI (60/40/10/40/5)	2260	1490
6.	MY720/Epon 828/TETA (60/40/17)	2150	1160
7.	EPN 1128/Epon 828/TETA/840 (60/40/10/40)	3130	1420
8.	EPN 1128/Epon 828/TETA/840/2, 4 EMI (60/40/10/40/4)	3010	1670
9.	EPN 1138/Epon 828/TETA (60/40/17)	2810	1580
10.	Epon 828/TETA/840 (100/10/40)	3280	630
11.	Epon 828/TETA/840/24EMI (100/8/40/5)	3080	870

TABLE 4: EFFECT OF 30 DAY WATER IMMERSION ON THE LAP SHEAR STRENGTH OF SOME ROOM TEMPERATURE CURING HIGH FUNCTIONALITY EPOXY RESIN SYSTEMS (2024 Aluminum alloy, FPL etch treatment)

EPOXY RESIN FORMULATION	After 30 days	
	Initial	Water Immersion
1. Epoxy Resin 0500/Epon 828/TETA/840 (60/40/12/40)	2590	2460
2. Epoxy Resin 0500/Epon 828/TETA/840/2, 4, EMI (60/40/10/40/4)	2670	2650
7. EPN 1138/Epon 828/TETA/840 (60/40/10/40)	3130	3090
8. EPN 1138/Epon 828/TETA/840/2, 4 EMI (60/40/10/40/4)	3080	1740
9. EPN 1138/Epon 828/TETA (60/40/12)	2810	1540

TABLE 5: EFFECT OF VARIOUS TEMPERATURE EXPOSURES ON THE LAP SHEAR STRENGTH OF TWO ROOM TEMPERATURE CURING HIGH FUNCTIONALITY EPOXY RESIN SYSTEMS (2024 Aluminum alloy, FPL etch treatment)

EPOXY RESIN FORMULATION	LAP SHEAR STRENGTH, PSI					
	-50 C (-60 F)	25 C (77 F)	120 C (250 F)	150 C (300 F)	200 C (394 F)	
7. EPN 1138/Epon 828/TETA/840 (60/40/10/40)	2960	3130	2840	1420	1040	
8. EPN 1138/Epon 828/TETA/840/ 2, 4 EMI(60/40/10/40/4)	3270	3080	2910	1670	1130	
9. EPN 1138/Epon 828/TETA (60/40/12)	3150	2810	2860	1580	1150	

performance. The lap shear strengths reported are therefore significantly lower than those which can be expected with suitably compounded resin formulations with state-of-the-art compounding these high functionality epoxy resin systems are thus quite likely to exhibit attractive properties for high performance bonding applications.

The test results are particularly impressive when they are compared with typical commercially offered room temperature curing adhesive systems. Table 6 compares the lap shear strength properties of a number of such commercially marketed structural adhesives with those obtained with the three typical room temperature curing high functionality epoxy resin systems developed in the course of this research. The commercial adhesives included so called reaction acrylic, anaerobic and epoxy types. For information purposes, lap shear strengths of a commercial vinyl ester type resin are also shown. Data are presented for the room temperature, 121 C (250 F) and 150 C (300 F) lap shear strengths. The three room temperature curing highly functional epoxy resin compositions are seen to have a significantly superior adhesive properties in terms of lap shear strength compared to the various room temperature cured commercial adhesives. The improved performance of these three high functionality epoxy resin composition at higher exposure temperatures, e.g., 121 C (250 F) and especially 150 (300 F) must be regarded as most noteworthy and certainly promising for further development.

A limited amount of work was also carried out on the study of the adhesion characteristics of high functionality epoxy resins when cured with selected hardeners at elevated temperatures. Such elevated temperature curing high functionality epoxy resin compositions are becoming widely accepted especially for their

reportedly excellent performance at high service temperatures. Reports indicate that they have superior lap shear strength properties upon very long exposures to temperatures as high as 200 C (394 F). The tests carried out confirm these claims. The room temperature curing high functionality epoxy resin compositions developed in this study have a definitely lower level of high temperature service capability, but offer definite processing advantages, etc. as desired. This is to be expected on the basis of earlier investigations in this field which indicate that the development of optimal high temperature strength properties requires that the resin be cured at some temperature above the proposed use temperature.

Exploratory experiments were also carried out on a comparison of the high temperature physical strength properties of glass fiber reinforced laminates prepared with high functionality epoxy resin formulations cured with suitable hardeners at elevated temperatures versus typical room temperature cured resin systems with high temperature service capability such as have been investigated in this study. Data are presented in Figure 36. They confirm the superior elevated temperature performance of the heat cured laminates, but with the room temperature cured adhesive compositions showing up surprisingly well. Further development and optimization of the concept of room temperature curing high functionality epoxy resin system appears very justified on the basis of these experimentally obtained physical strength measurements at elevated temperatures.

TABLE 6: LAP SHEAR STRENGTH OF TYPICAL HIGHLY FUNCTIONAL ROOM TEMPERATURE CURING EPOXY RESIN COMPOSITION AND SELECTED ROOM TEMPERATURE CURING COMMERCIAL ADHESIVES AT 25 C (77 F), 121 C (250 F) and 150 C (300 F)

		(2024 Aluminum alloy, FPL etch)		LAP SHEAR STRENGTH		
				PSI		
		Manufac-turer		25 C (77 F)	121 C (250 F)	150 C (300 F)
		Adhesive Type				
ADHESIVE COMPOSITION	EPN 1138/Epon 828/TETA/840 (60/40/12/40)	RT cure epoxy	NYU	3130	2840	1420
	EPN 1128/Epon 828/TETA/840/2,3 EMI (60/40/10/40/4)	RT cure epoxy	NYU	3080	2910	1670
	EPN 1138/Epon 828/TETA (60/40/17)	RT cure epoxy	NYU	2810	2860	1580
	Quickbond 610	RT cure acrylic	Permabond	1466	640	<100
	R0018	RT cure acrylic	Fuller	3140	720	<100
	Versilock 513	RT cure acrylic	Hughson	2480	310	<100
	Speedbonder 306	RT cure anaerobic	Loctite	1510	530	<100
	Speedbonder 324	RT cure anaerobic	Loctite	2870	150	-
		" "	Loctite			
	Weldmaster 3	RT cure acrylic	National Starch	3920	470	<100
	RP 136	RT cure epoxy	Ren	1520	280	-
	Epocryl 480	Vinyl ester, RT cured	Shell	1390	760	275
Diacryl 101	Acrylic, RT cured	AKZO	2870	1135	180	

III. DISCUSSION AND CONCLUSIONS

Room temperature curing polymer systems with high temperature service capability can offer significant processing advantages including energy savings and simplified repairs for the manufacture and use of fiber reinforced composites, adhesives and sealants in both aerospace and industrial applications. This report describes the development and preliminary evaluation of novel room temperature curing two component high functionality epoxy resin compositions with high temperature service capability with emphasis on the preparation of glass fiber cloth reinforced laminates and, to a lesser extent, adhesives. The technical data obtained can obviously be applied to other types of reinforcements such as for example, graphite fibers and Kevlar aramid fibers in various forms. The specific formulations described must be regarded as model compositions and can no doubt be substantially improved by the application of the state-of-the-art compounding technology available today.

The various room temperature curing high functionality epoxy resin systems which have been experimentally studied are comprised of a multifunctional epoxy resin either as such or in a blend with a conventional bisphenol A type epoxy (component A) and a complex two or three component curing agent a particularly useful ingredient of which is an imidazole compound (component B). The pot life of these two component epoxy resin systems can be widely varied depending upon the types and amount of the components of the curing agent. Glass fiber cloth reinforced laminates were made by impregnating 181 style Volan A treated glass fiber cloth with such epoxy resins and curing the wet lay-ups at room temperature with pressure applications in the order of only 15 psi. Adhesive test specimens were prepared using 2024 aluminum alloy test coupons in lap shear strength configurations.

Measurements of the physical strength properties of the room temperature cured laminates after exposure to elevated temperatures as high as 200 C (394 F) for varying time periods up to 28 days were carried out. The test data showed surprisingly good performance. Those high functionality resin formulations which contained the imidazole compound in the curing agent exhibited markedly superior high temperature strengths compared to analogous compositions prepared without the imidazole. The specific test data developed thus far do not permit a choice between the high temperature behaviour of the three high functionality epoxy resins used per se or in the preparation of blends for this study, namely, MY 720, EPN 1138 and Epoxy Resin 0500. The work carried out furthermore shows that considerable latitude is available to the formulation of such resin compositions so as to best meet specific processing and performance requirements. It is believed that the development of improved high temperature properties is due to thermal activation of the curing agent as the laminates are heated. Although the role of imidazole as effective curing agents and hardeners for epoxy resins has long been recognized, the beneficial effects of such compounds as shown in this investigation are not fully understood. Development of prepreg systems with prolonged storage life without the need for refrigeration appears feasible with further formulation studies with catalysts such as DMHDA.

The resistance of such room temperature cured glass fiber reinforced laminates to water exposures has been studied. Test data showing the effect of water boiling up to 8 hours on physical strength properties have been obtained. They indicate a beneficial action of the imidazole -- albeit to a lesser extent than in the high temperature test program. Data have also been developed on the effect of laminate properties of longer term water -- immersions at room temperature. The experimental work suggests that the inclusion of an imidazole

component in the room temperature curing high functionality epoxy resin systems studied can substantially upgrade their high temperature and chemical resistance performance when used as matrix resins for the preparation of fiber reinforced laminates.

The applicability of these room temperature curing high functionality epoxy resin systems for the formulation of structural adhesives has also been investigated. Lap shear strength tests with 2024 aluminum test coupons were employed for this purpose using the highly functional epoxy resin systems for bonding at essentially contact pressures only. The results obtained show that these resin systems can offer remarkably attractive adhesive performance over the exceptionally wide service temperature range of -50°C (-60°F) to $+200^{\circ}\text{C}$ (394°F) especially when compared with the properties of various other commercially available room temperature curing adhesives. Water resistance data are likewise quite encouraging. This work is particularly promising because the test data recorded were obtained with the raw resins only rather than with the application of the extensive state-of-the-art compounding technology which is employed today for the formulation of commercial adhesives. Such reformulation with fillers and other additives can be expected to substantially upgrade their adhesive performance.

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- 2) Lee, H. and Neville, K.; "Epoxy Resins," McGraw Hill Publ. Co., New York, N.Y. (1957).
- 3) Graham, J.A.; USP 4,002,599 (1977); see also Graham, J.A. and O'Conner, J.E.; Adhesives Age, July 1978, p. 20-23.
- 4) Technical bulletin, "Epoxy Resin 0500," Ciba Geigy Corporation, Ardsley, New York (1978).
- 5) Rinde, J.A. and Newey, H.A.; SAMPE Journal (1979).

FIGURE 1

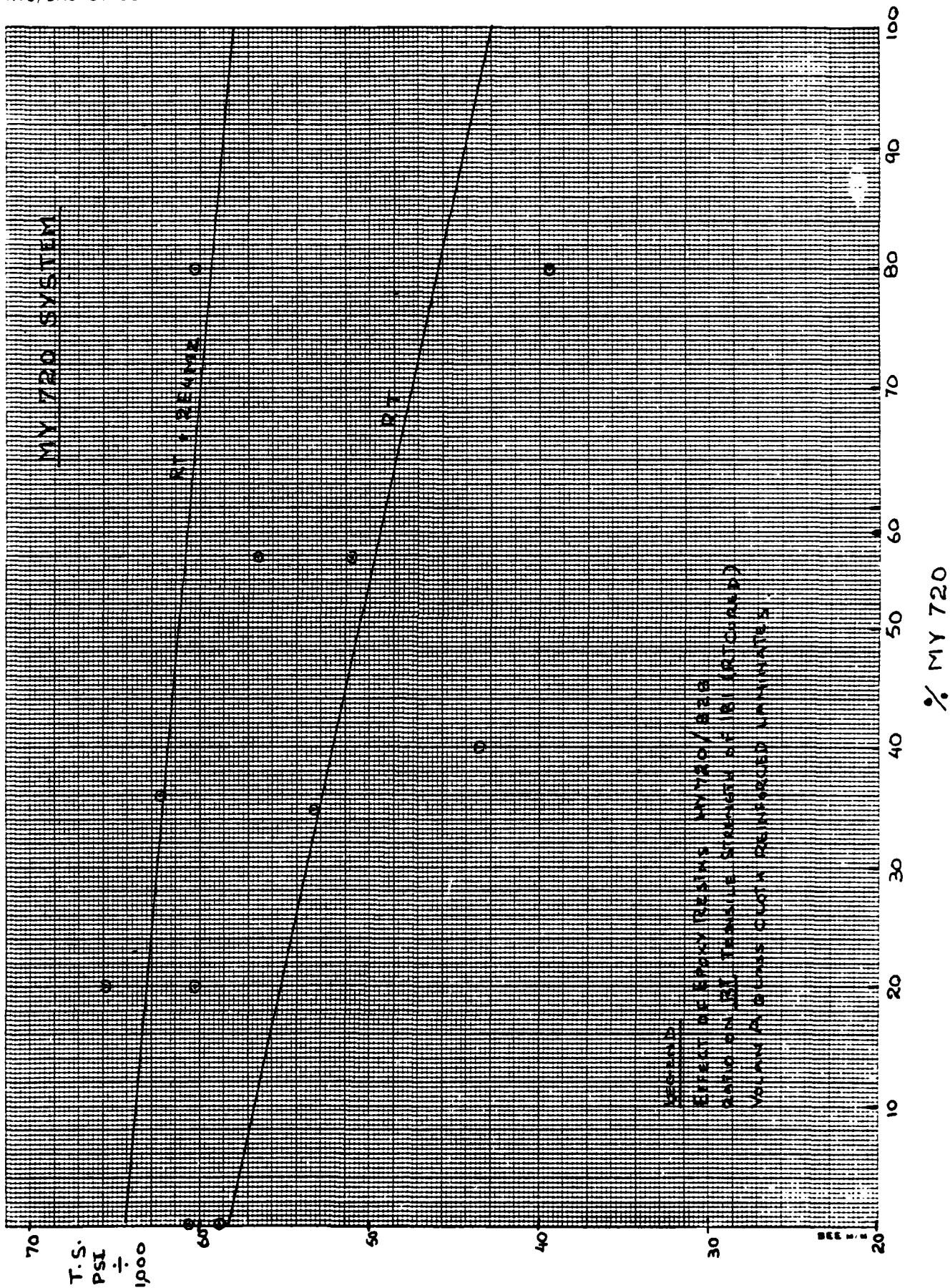


FIGURE 2

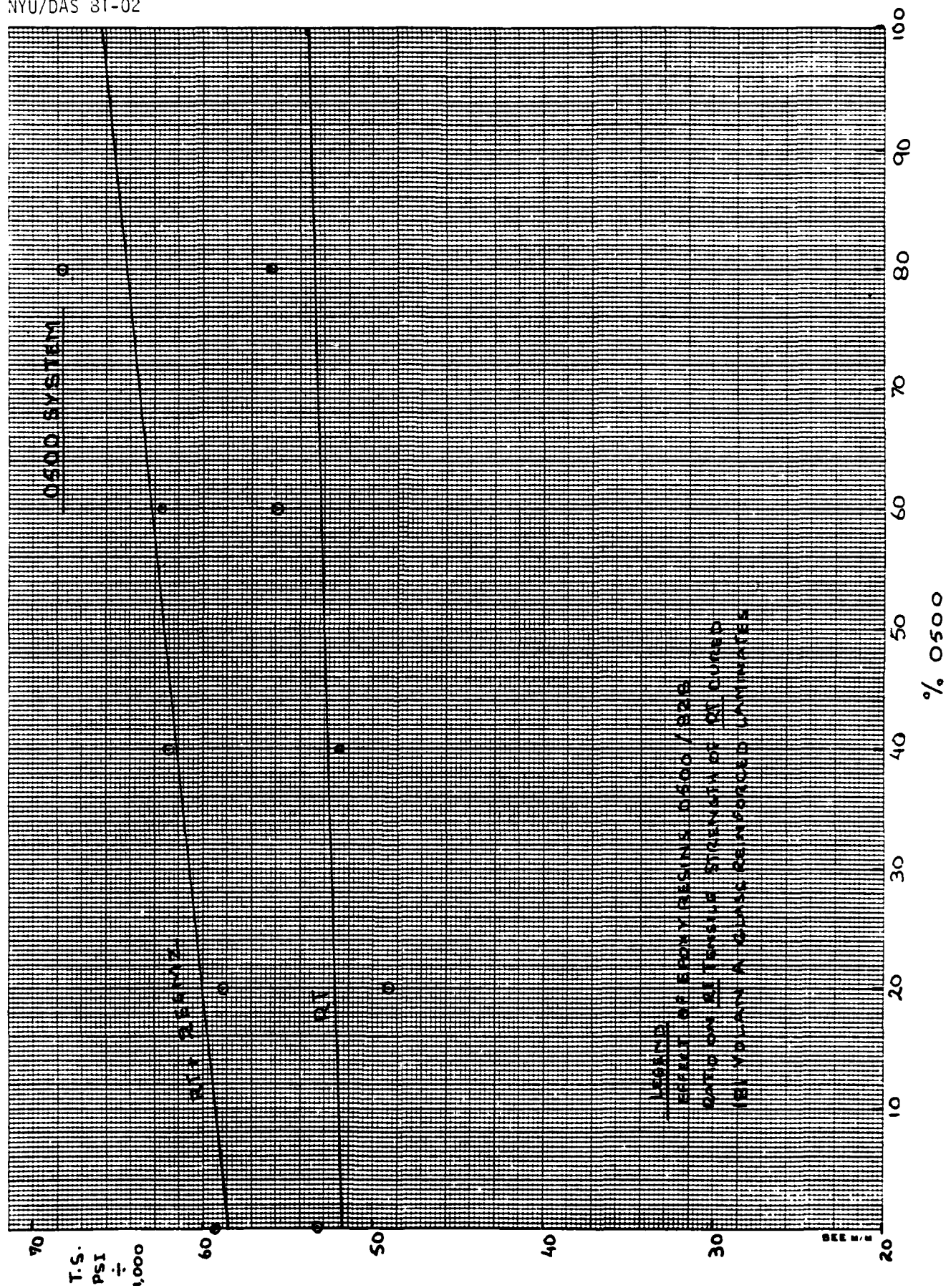


FIGURE 3

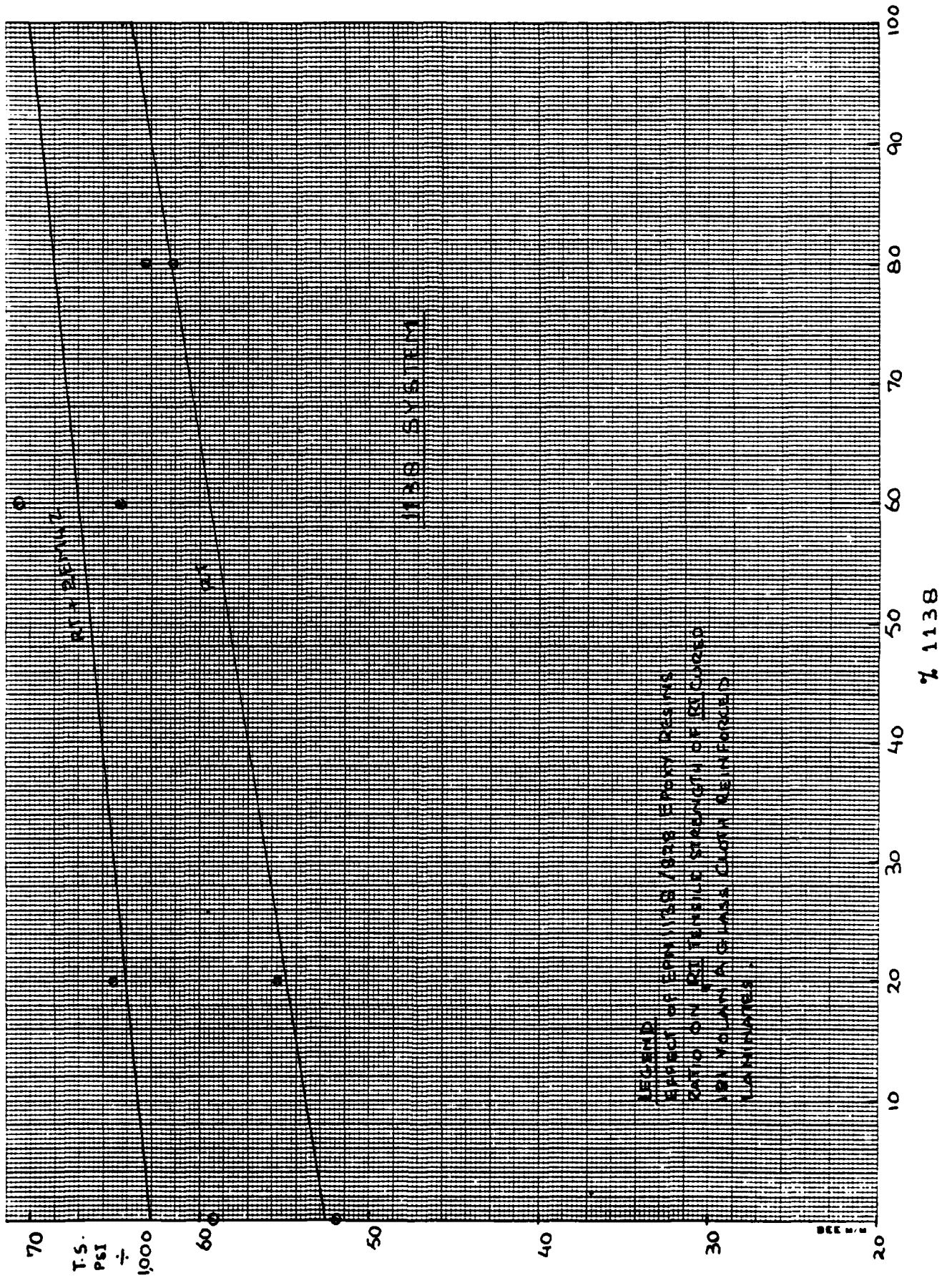


FIGURE 4

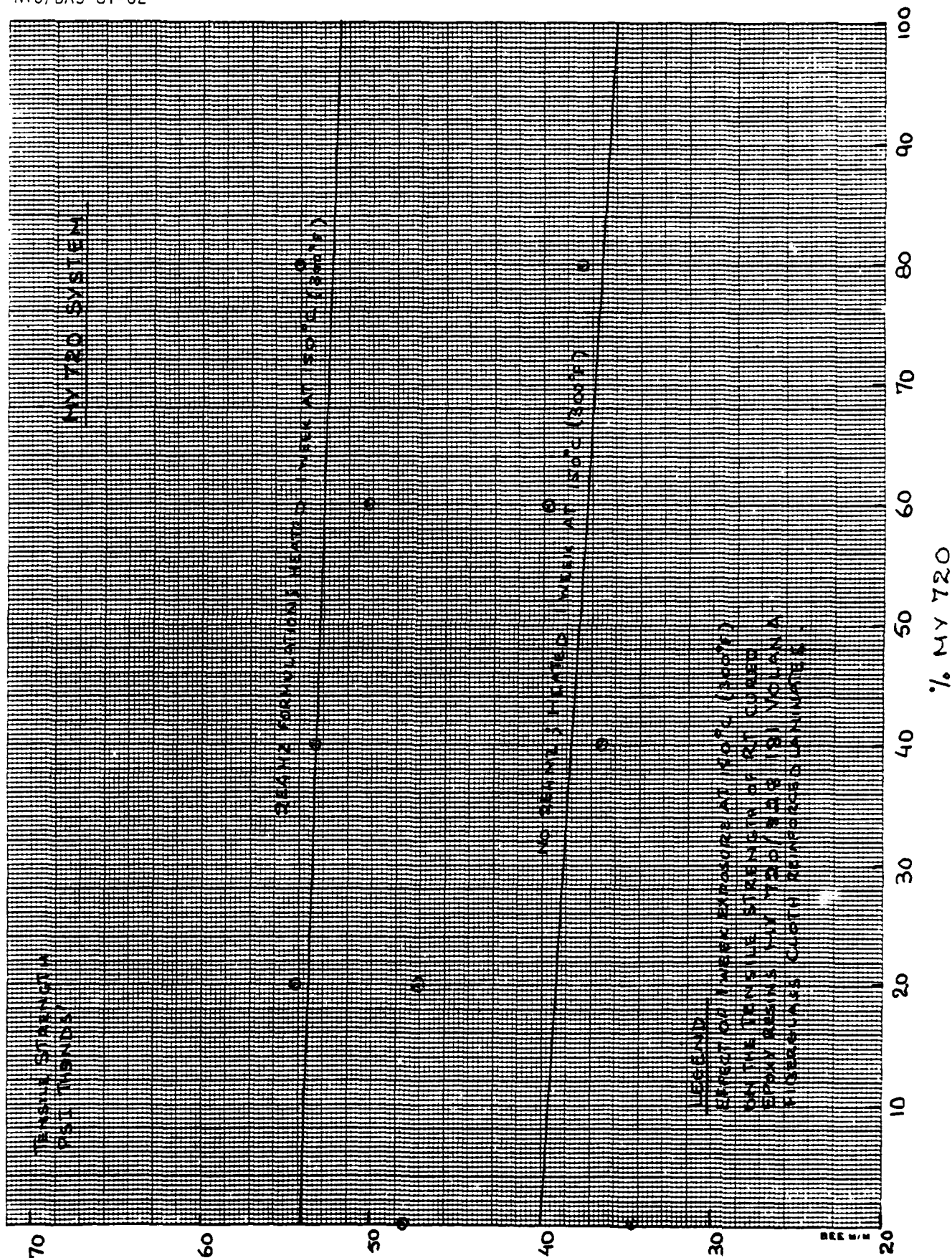


FIGURE 5

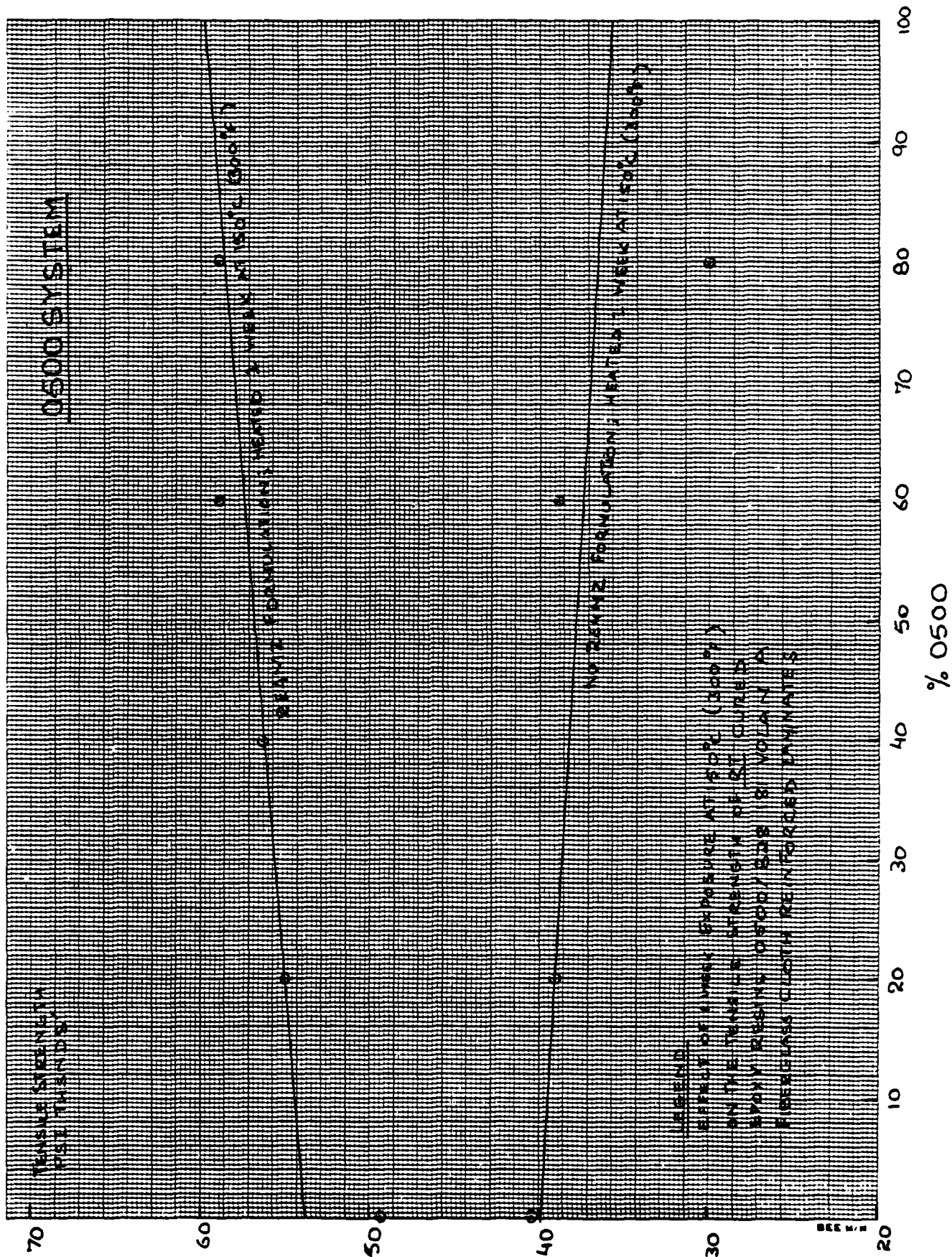


FIGURE 6

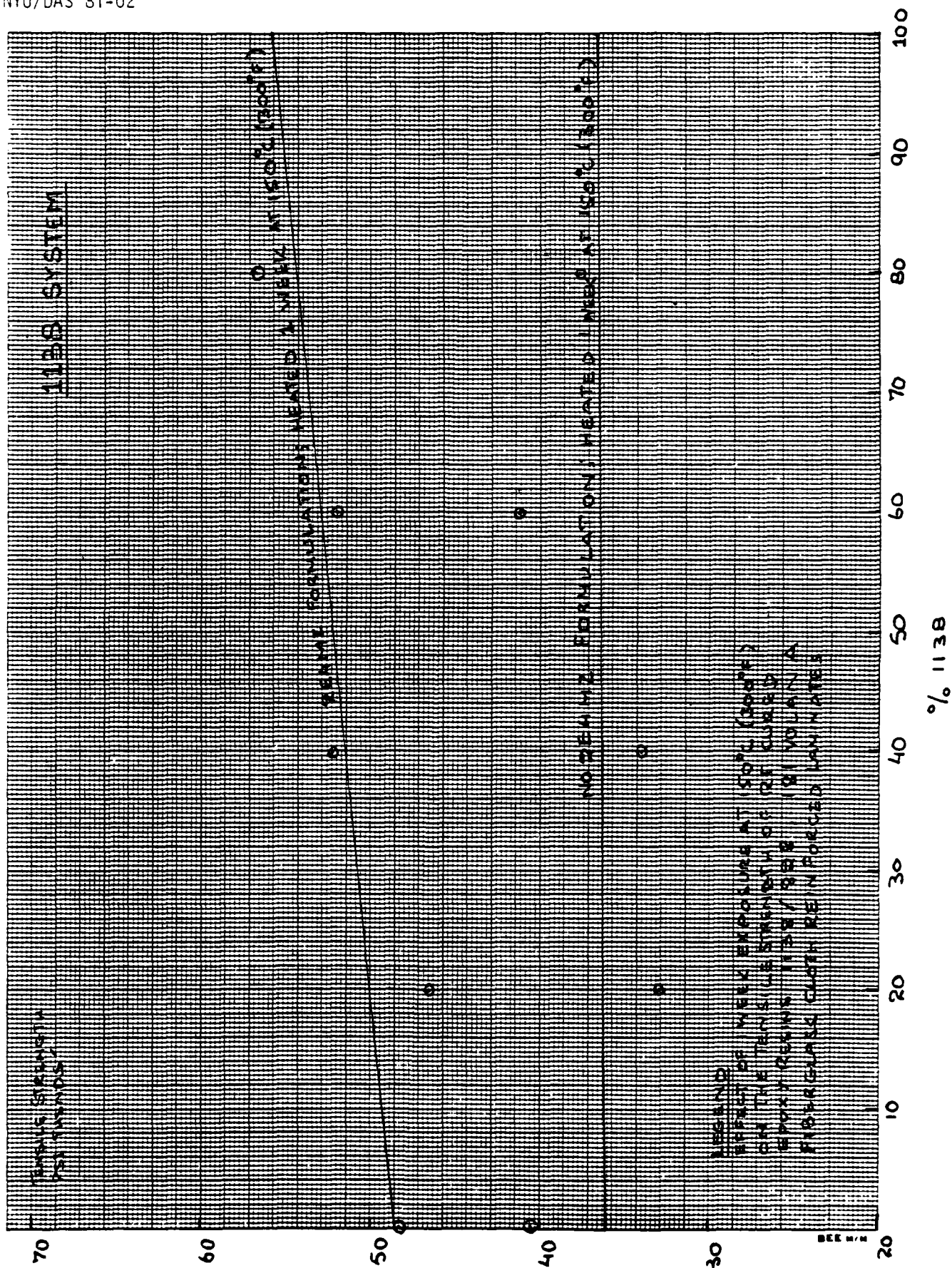


FIGURE 7

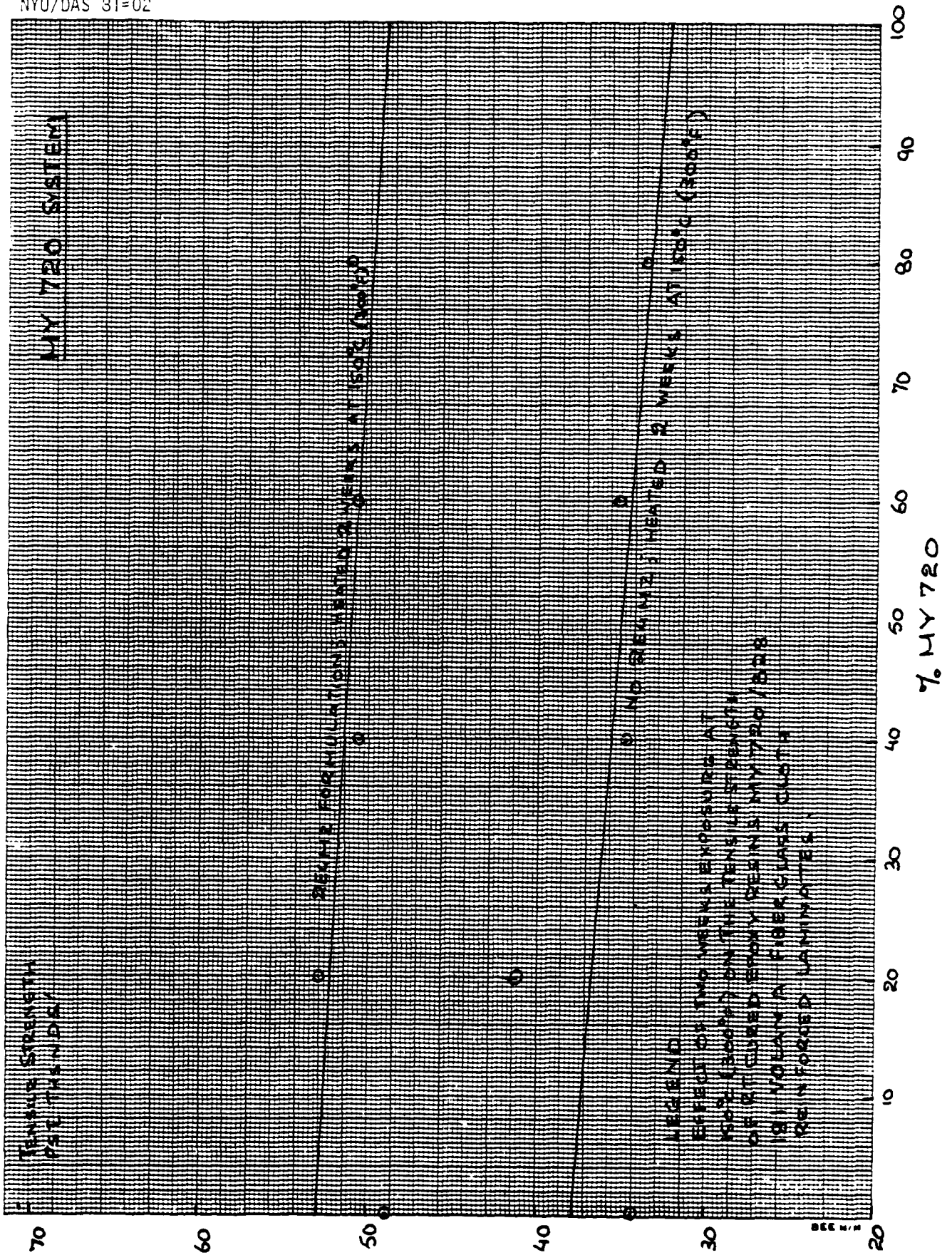


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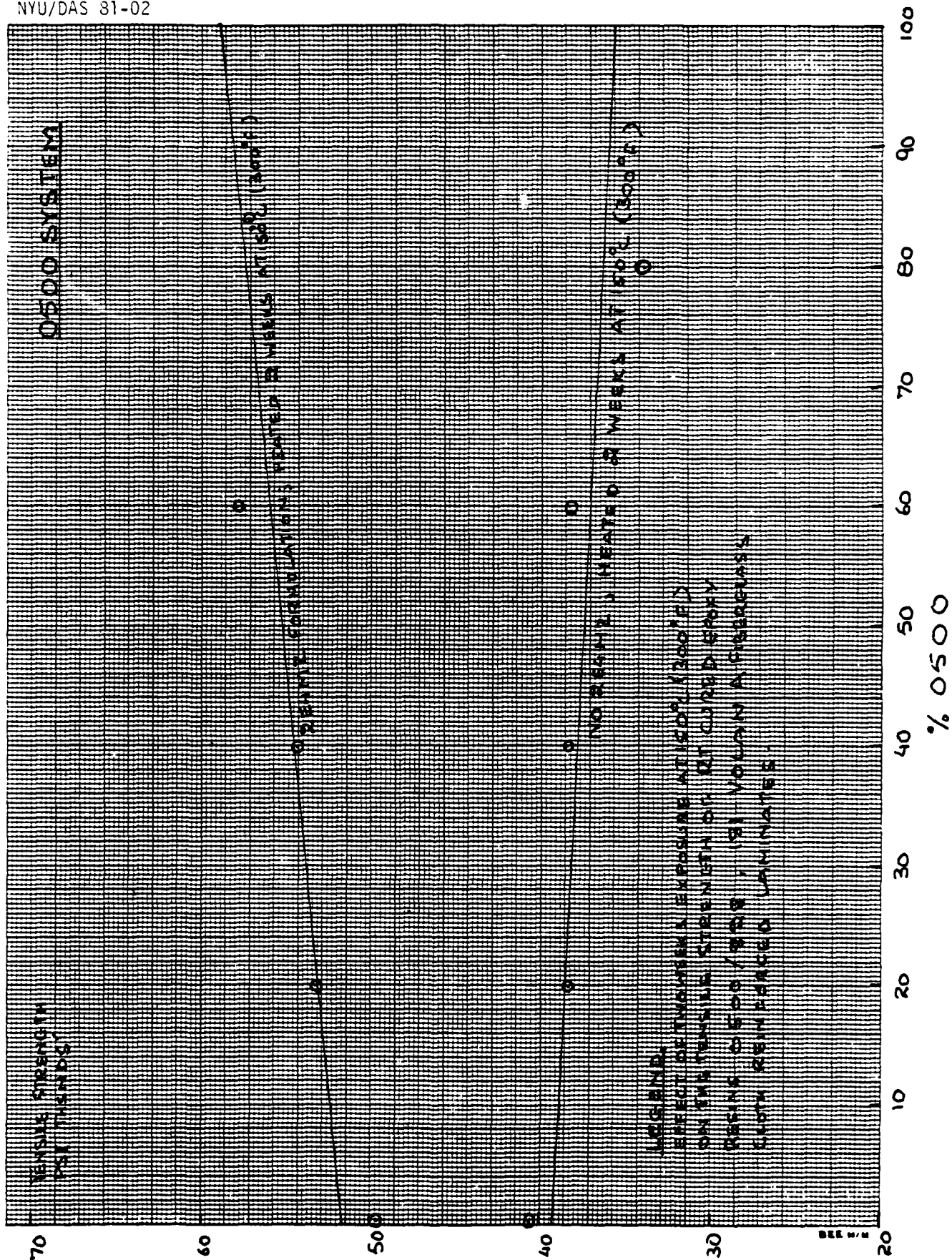


FIGURE 9

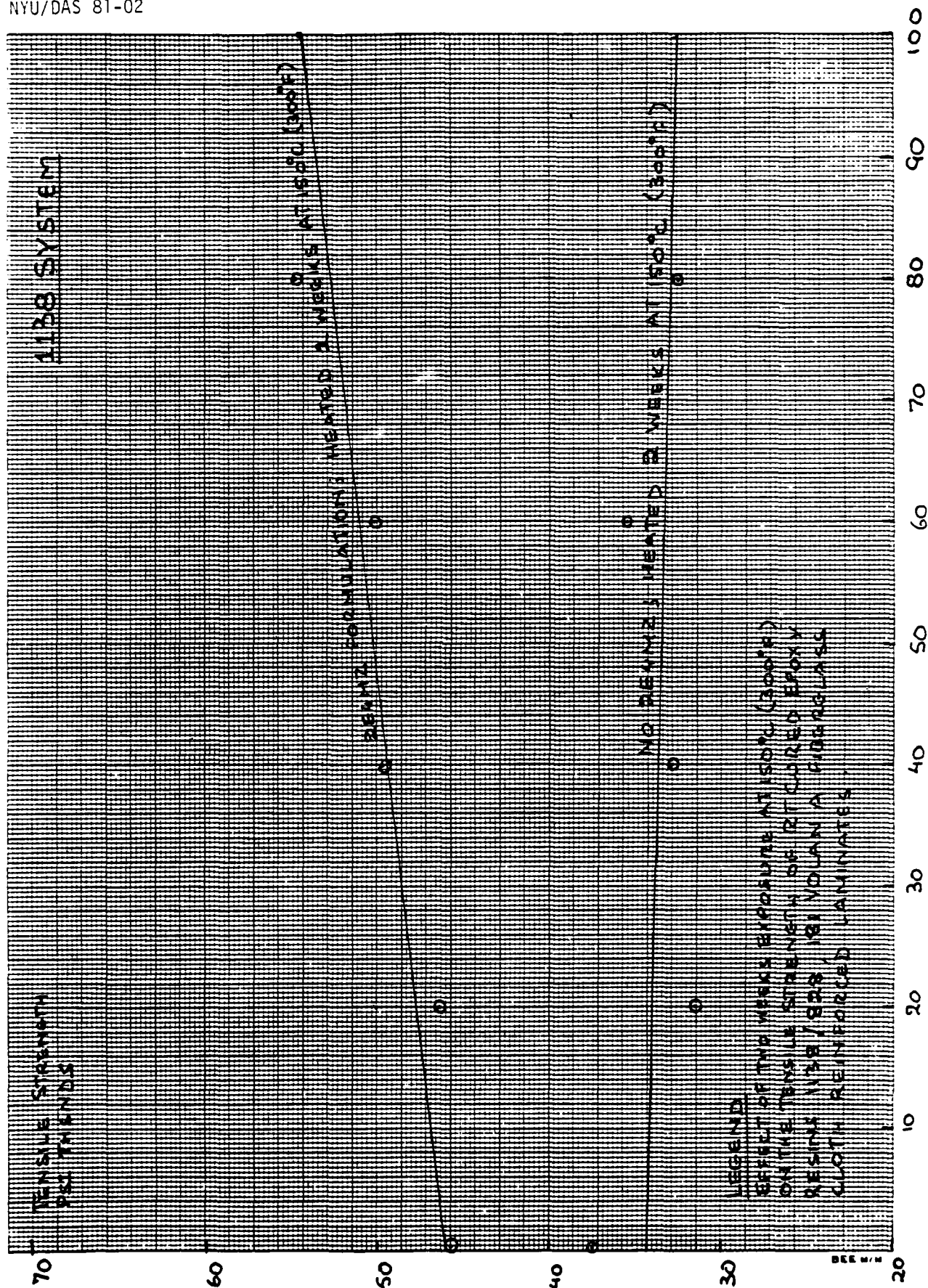
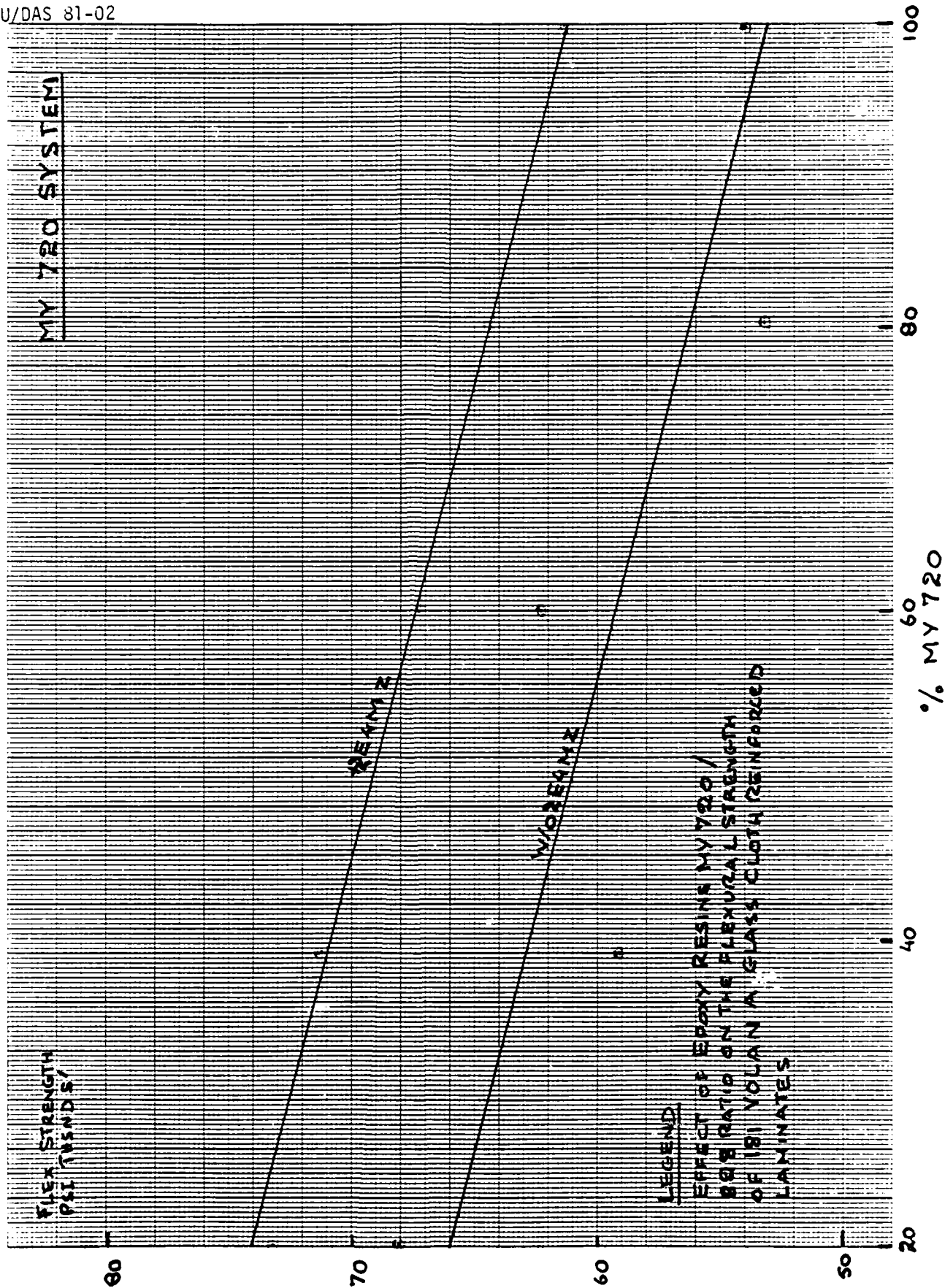


FIGURE 10



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FIGURE 11

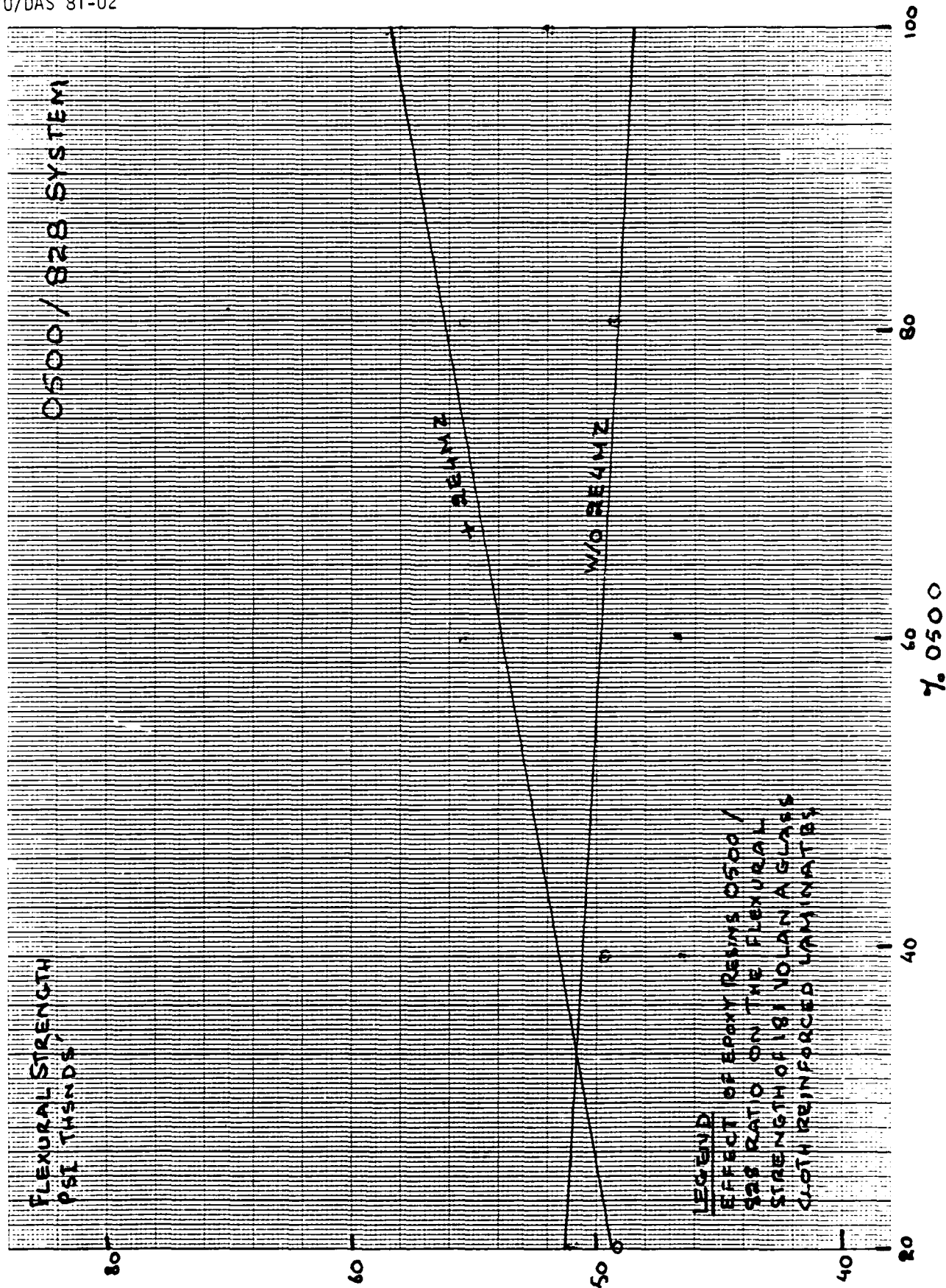
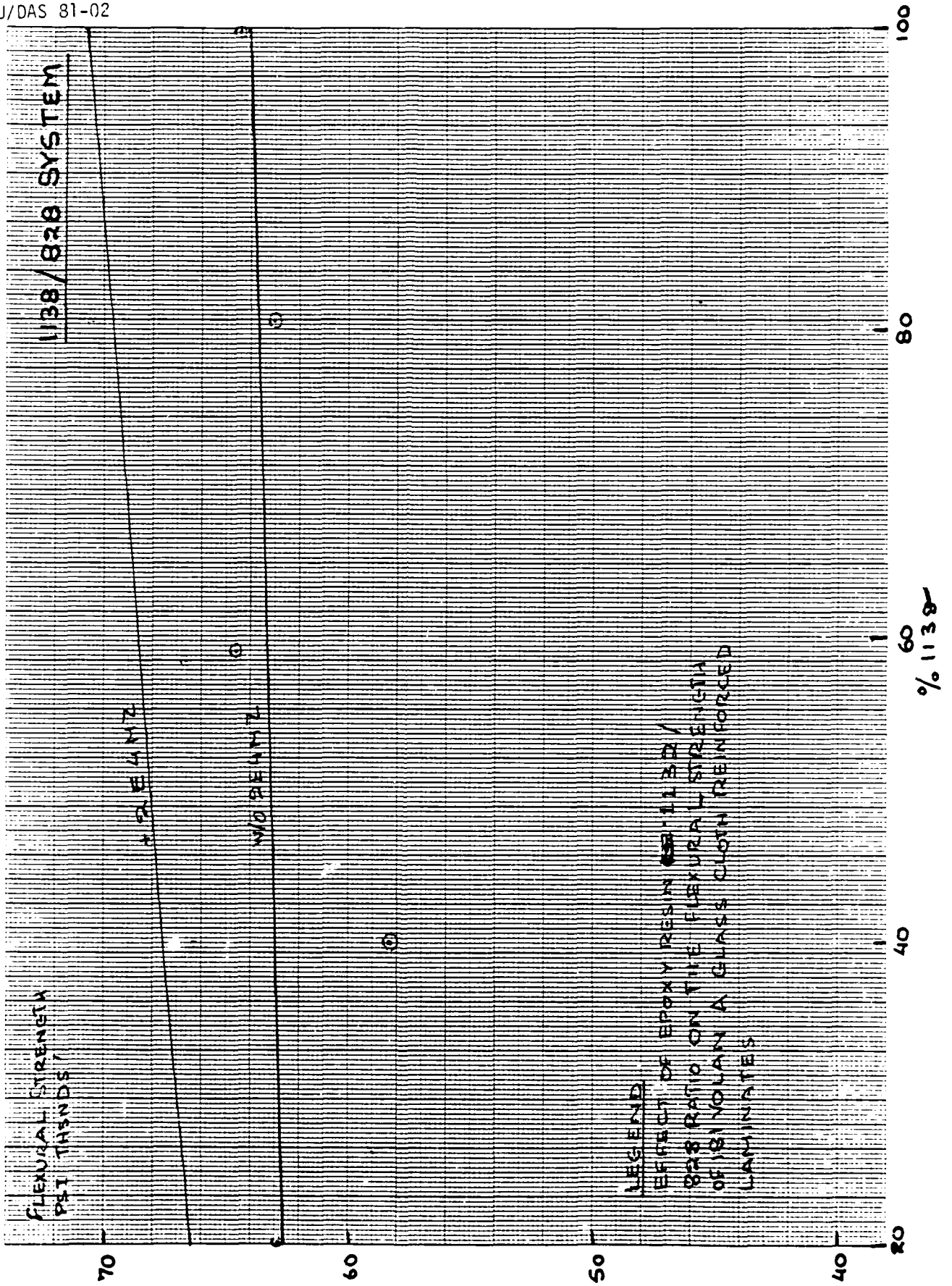


FIGURE 12



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REX, D&M TO THE COMMANDER, U.S. NAVY
REX, FLEET AIRCRAFT CARRIER

FIGURE 13

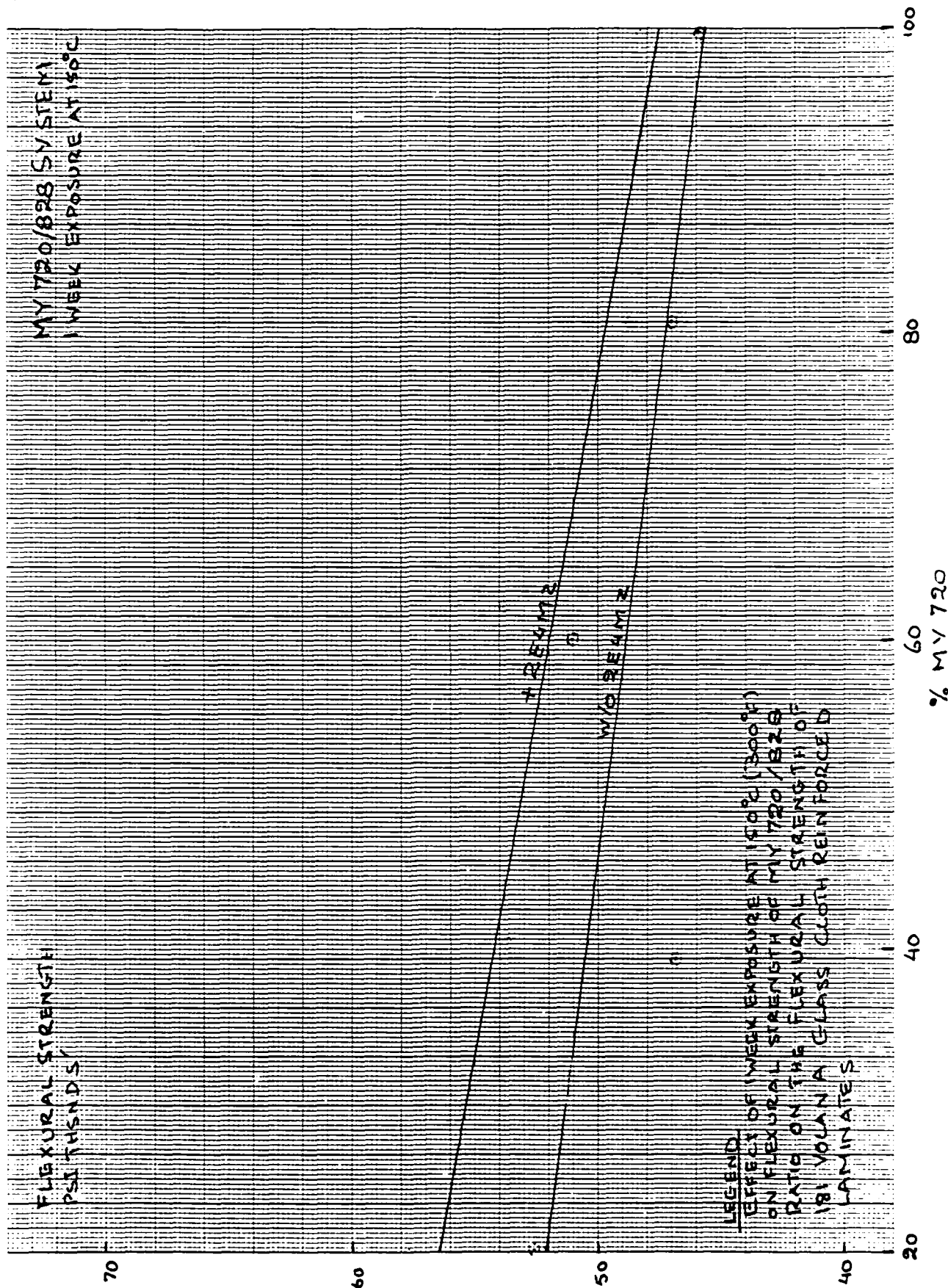
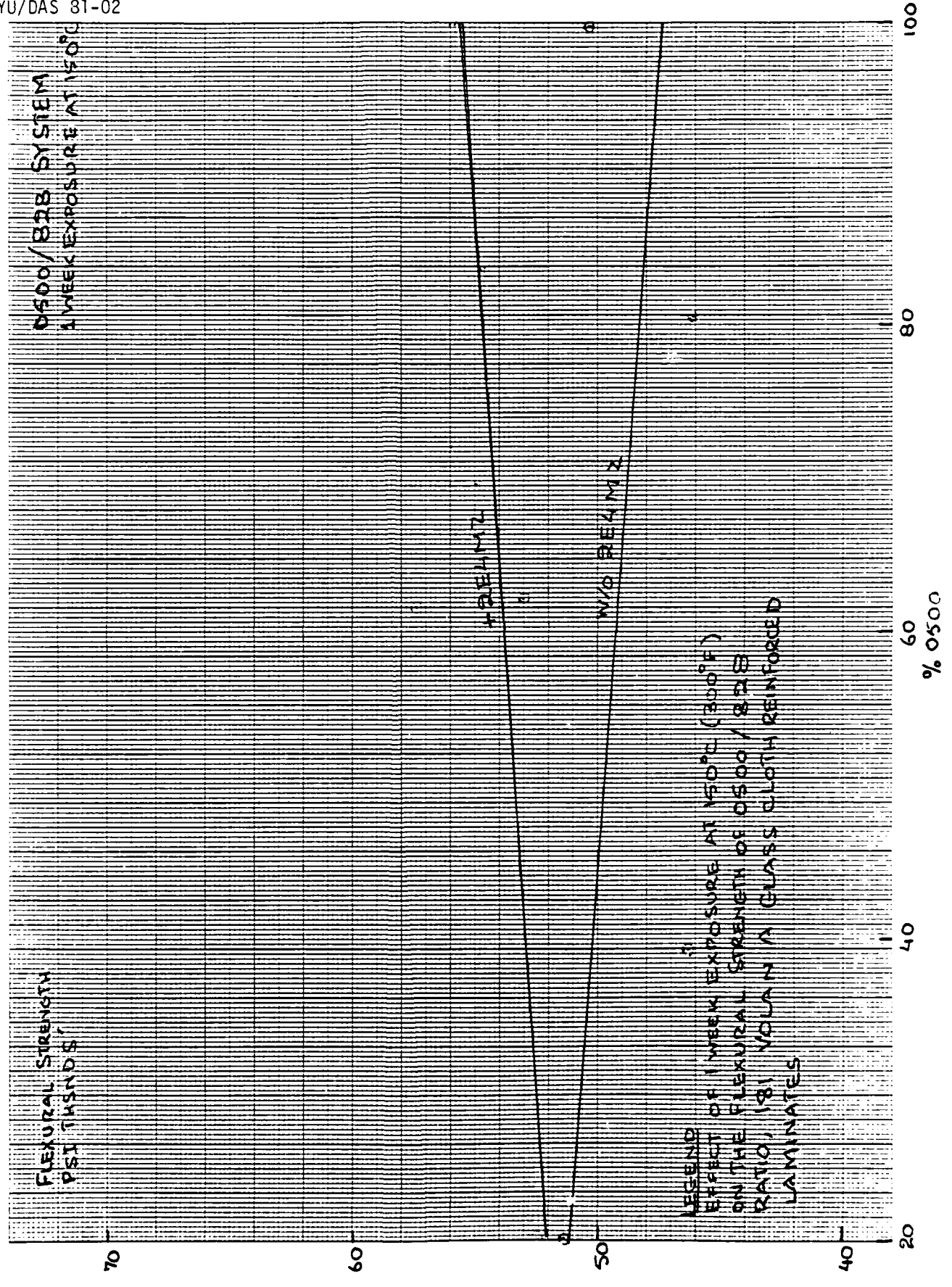
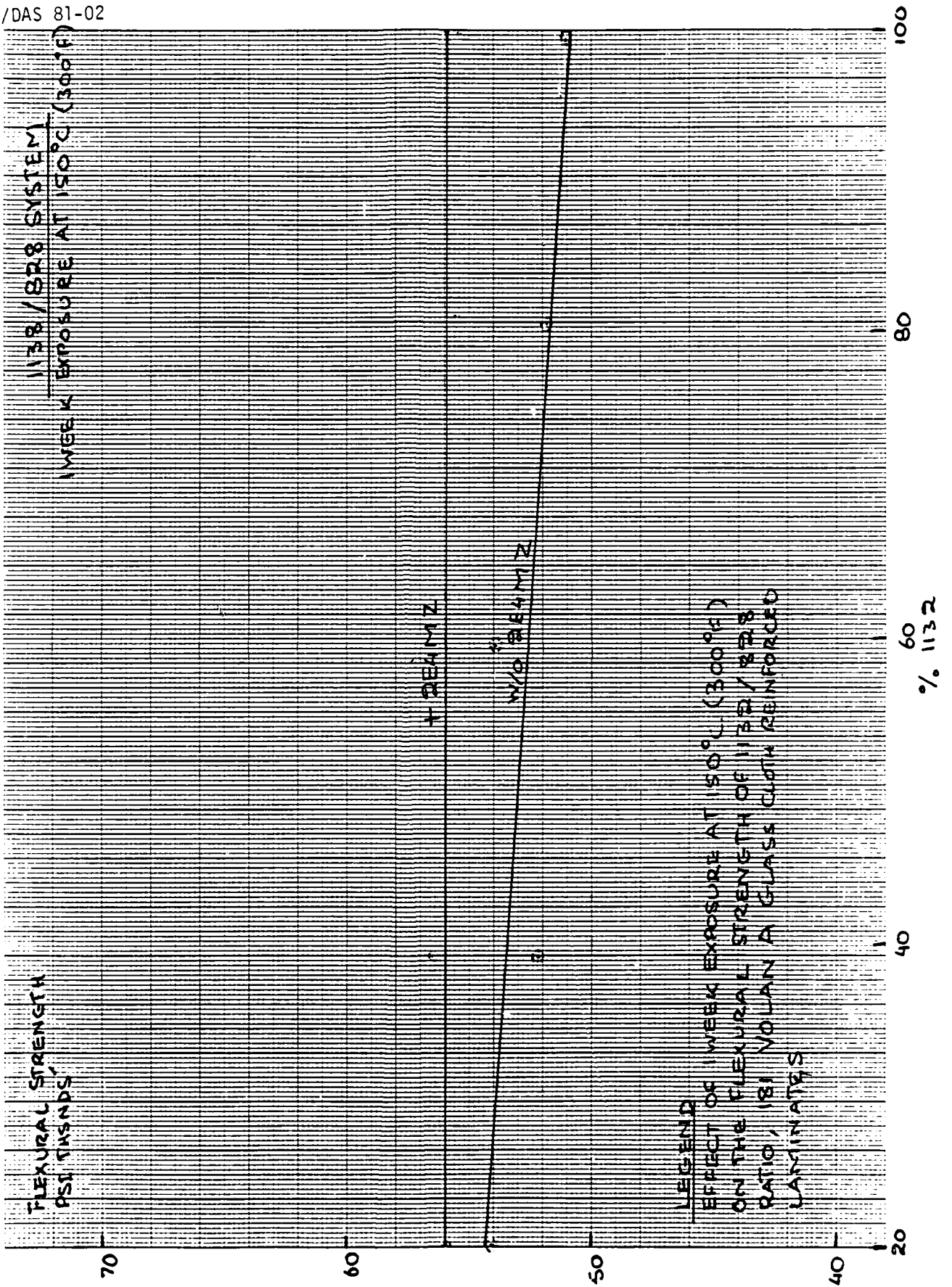


FIGURE 14



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FIGURE 15



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FIGURE 16

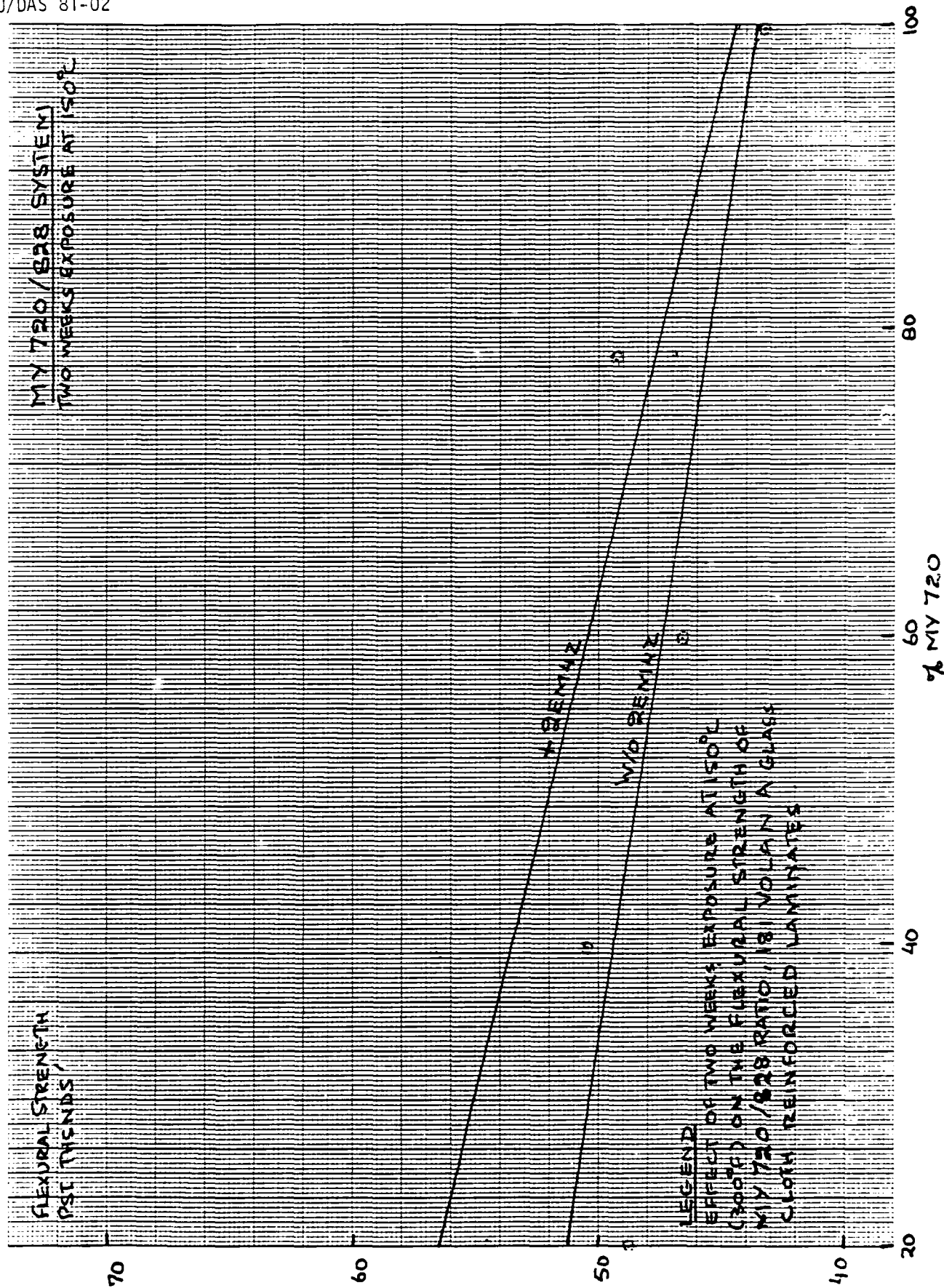
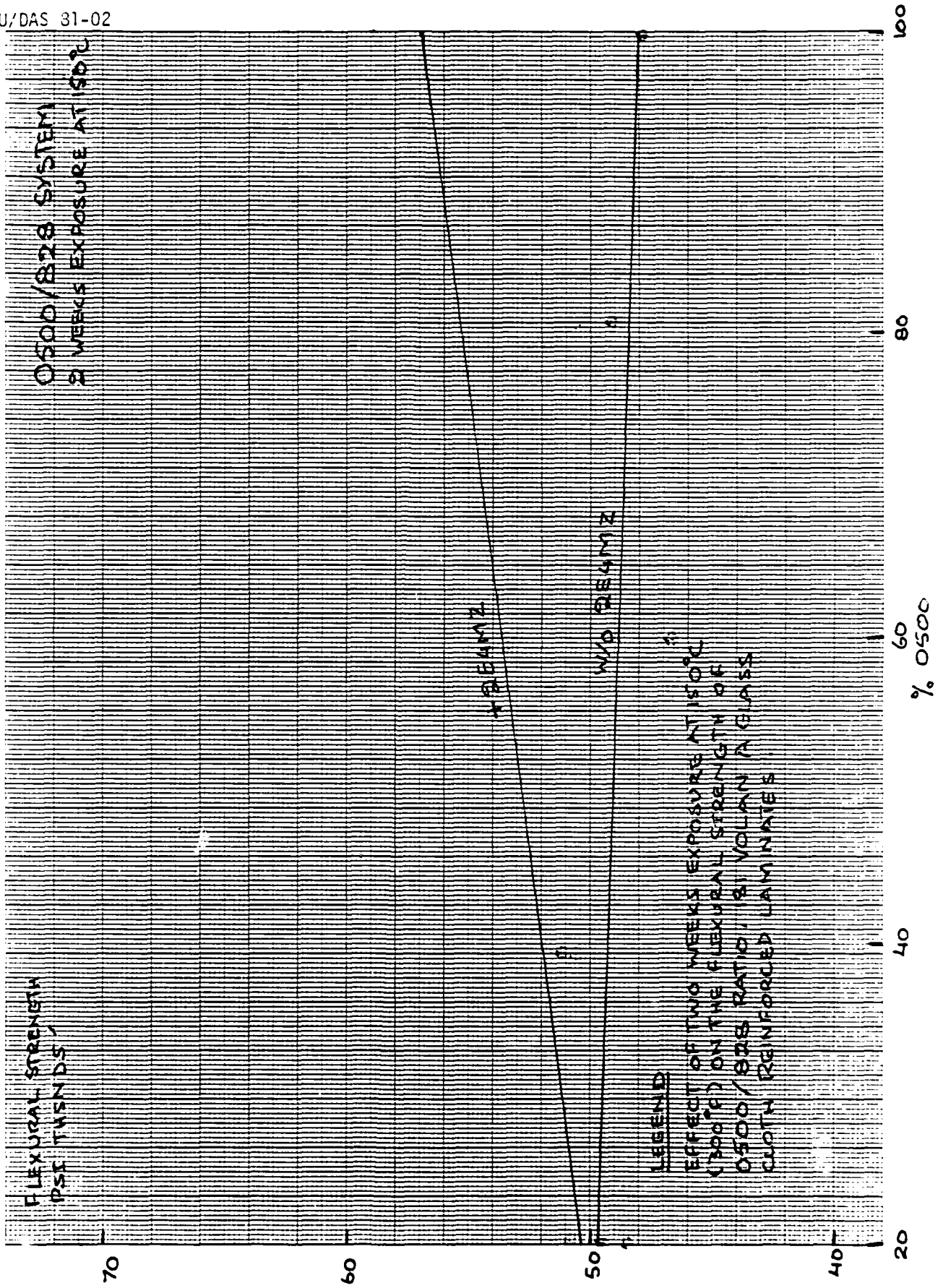
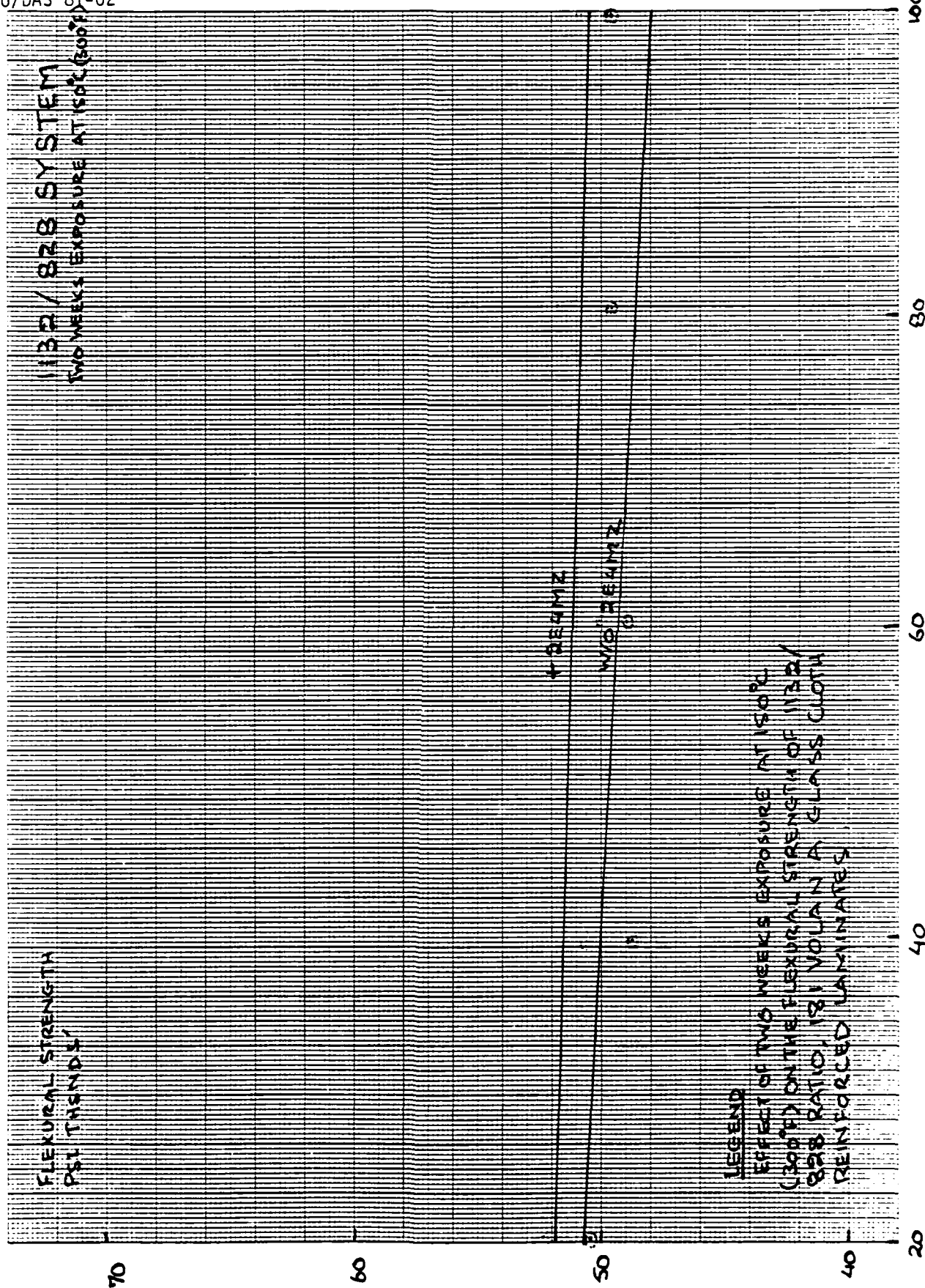


FIGURE 17



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FIGURE 18



60
7.1132

FIGURE 19

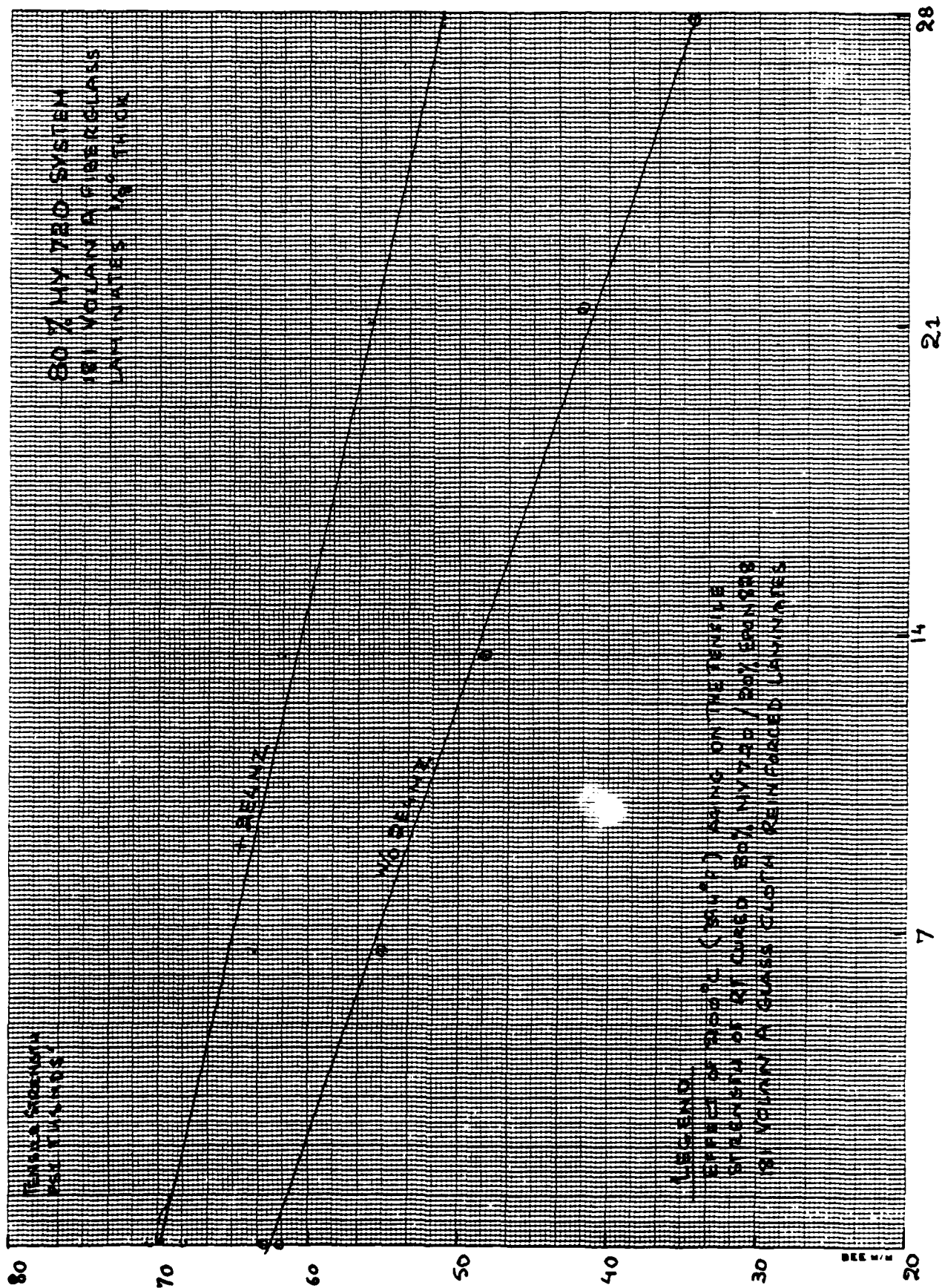


FIGURE 20

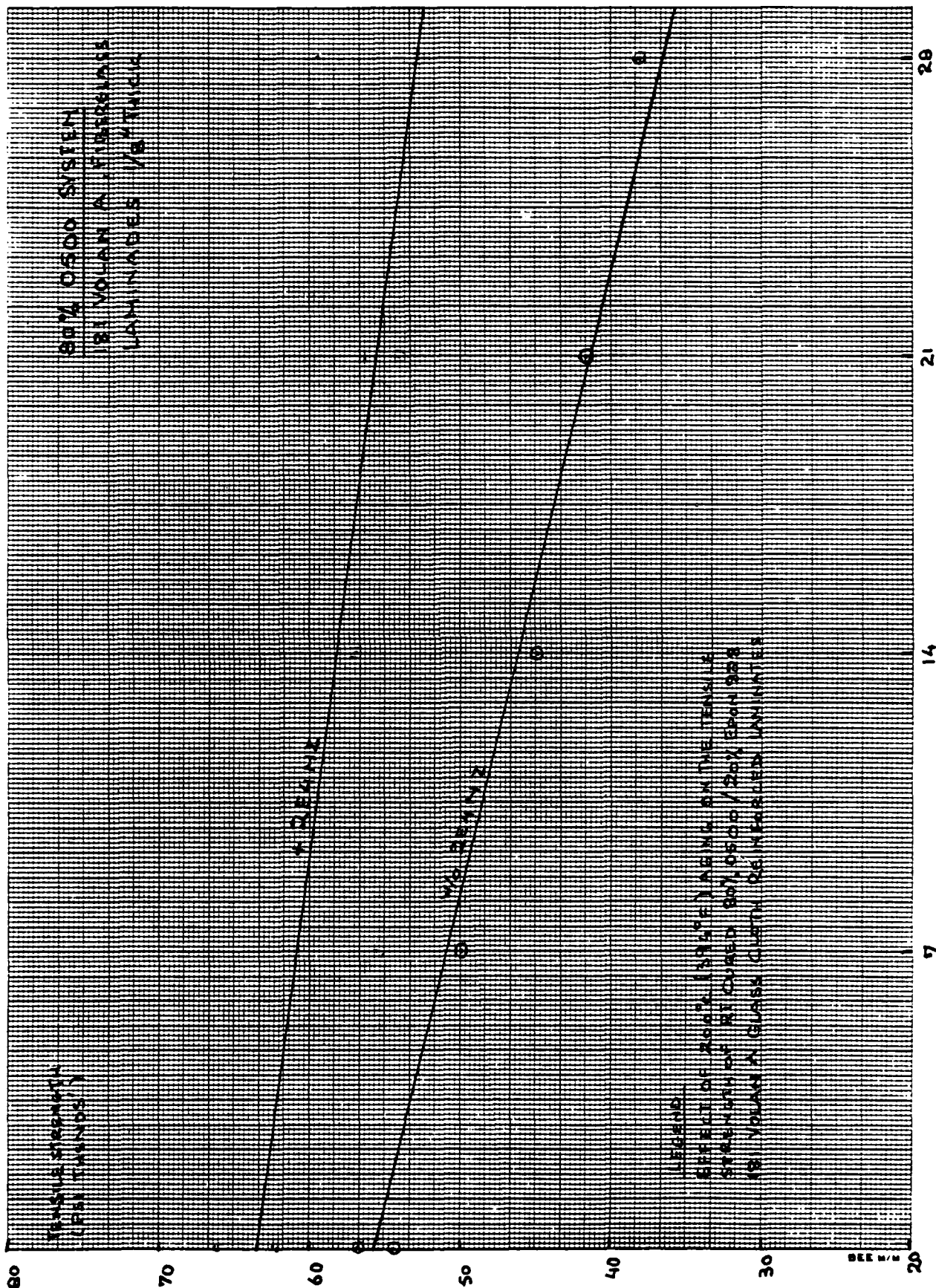


FIGURE 21

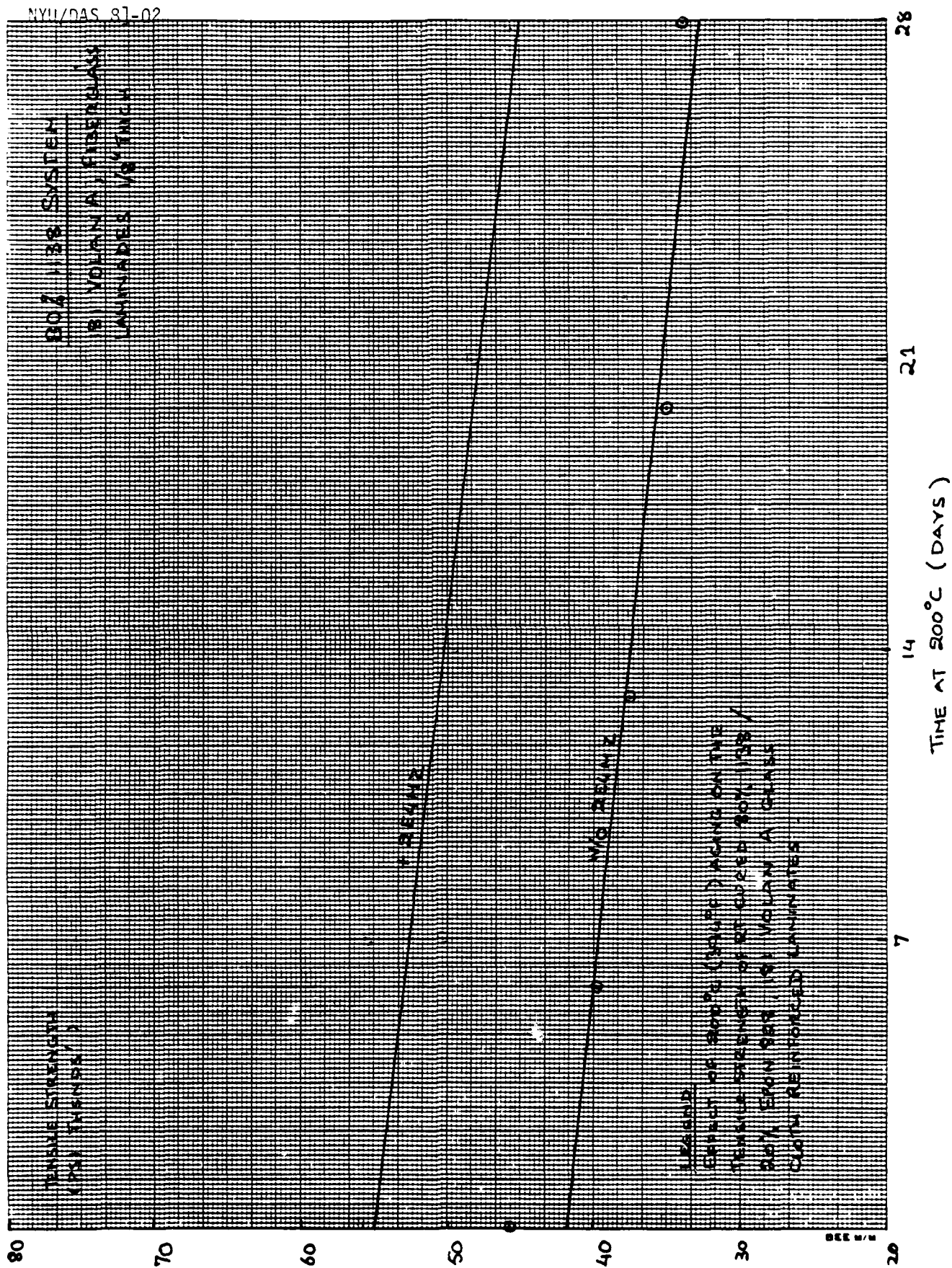
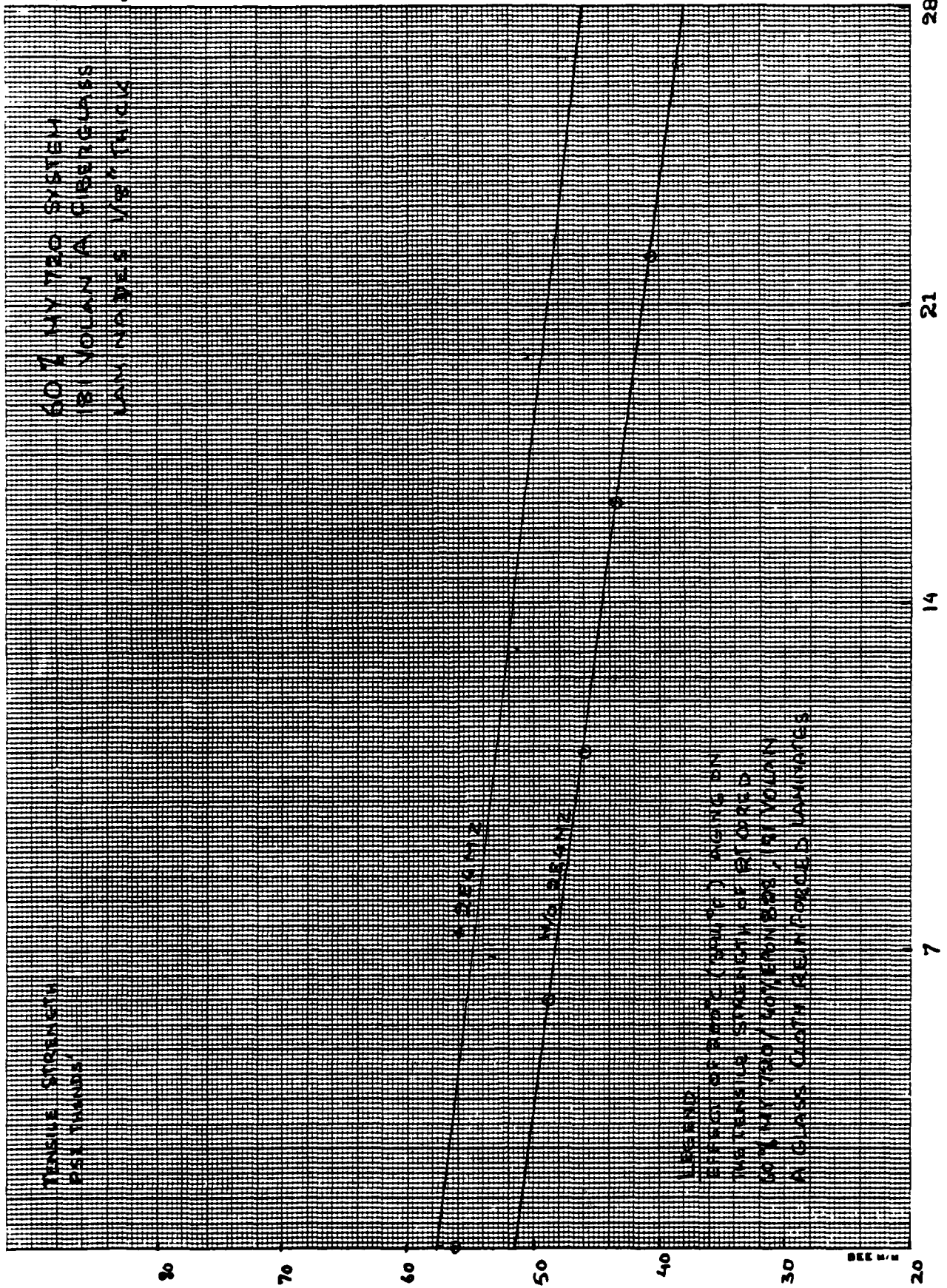


FIGURE 22



TIME AT 200°C (DAYS)

FIGURE 23

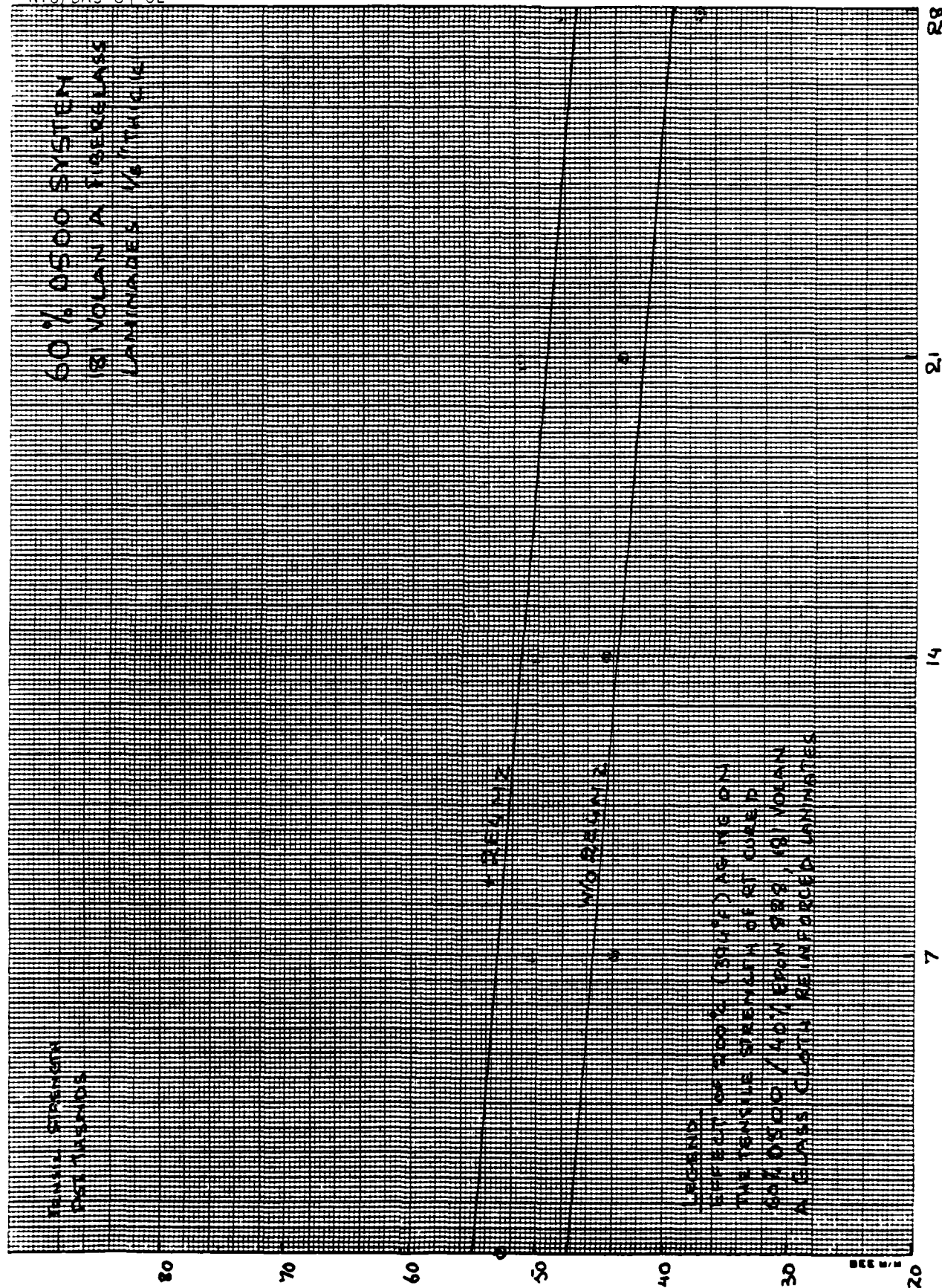


FIGURE 24

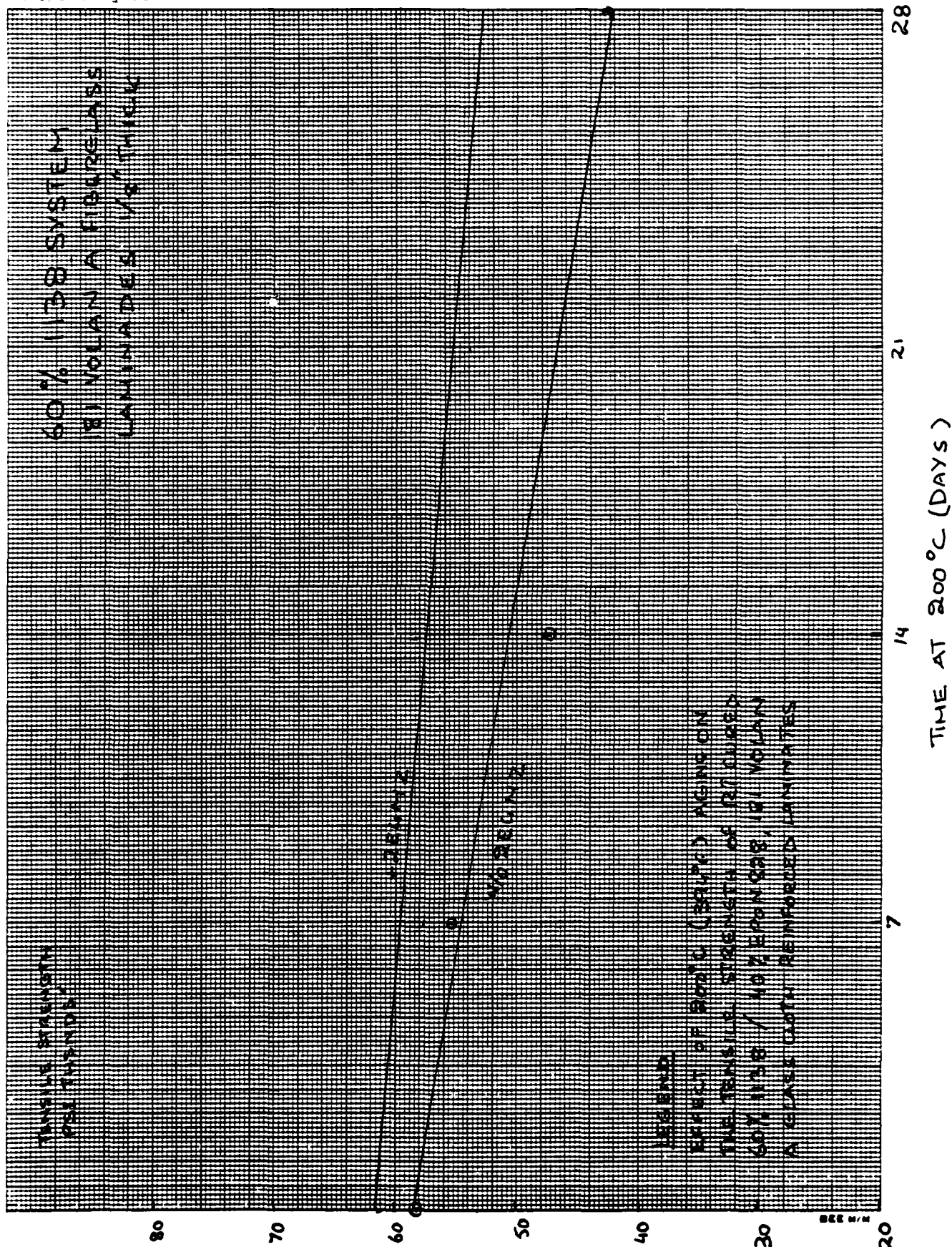


FIGURE 25

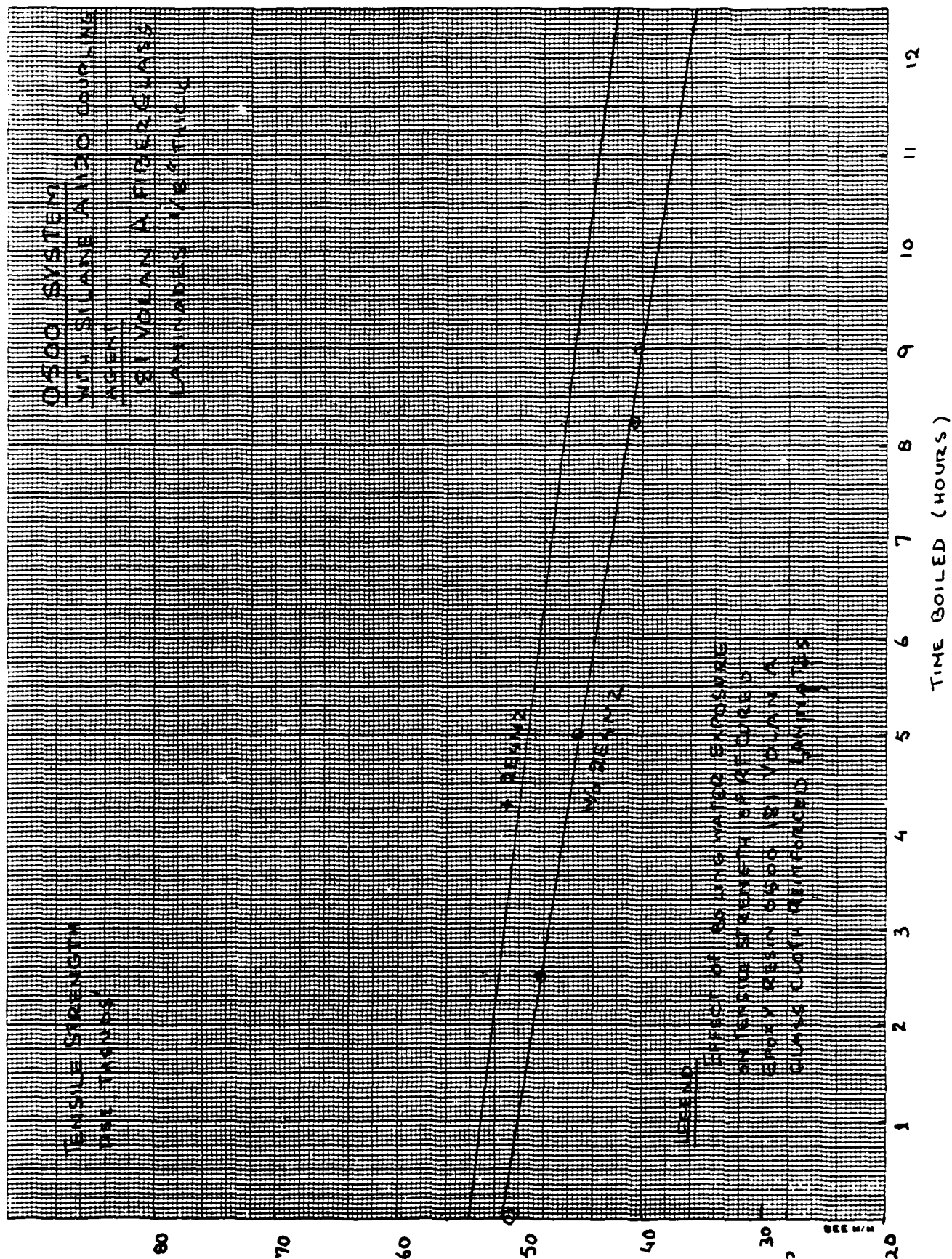


FIGURE 26

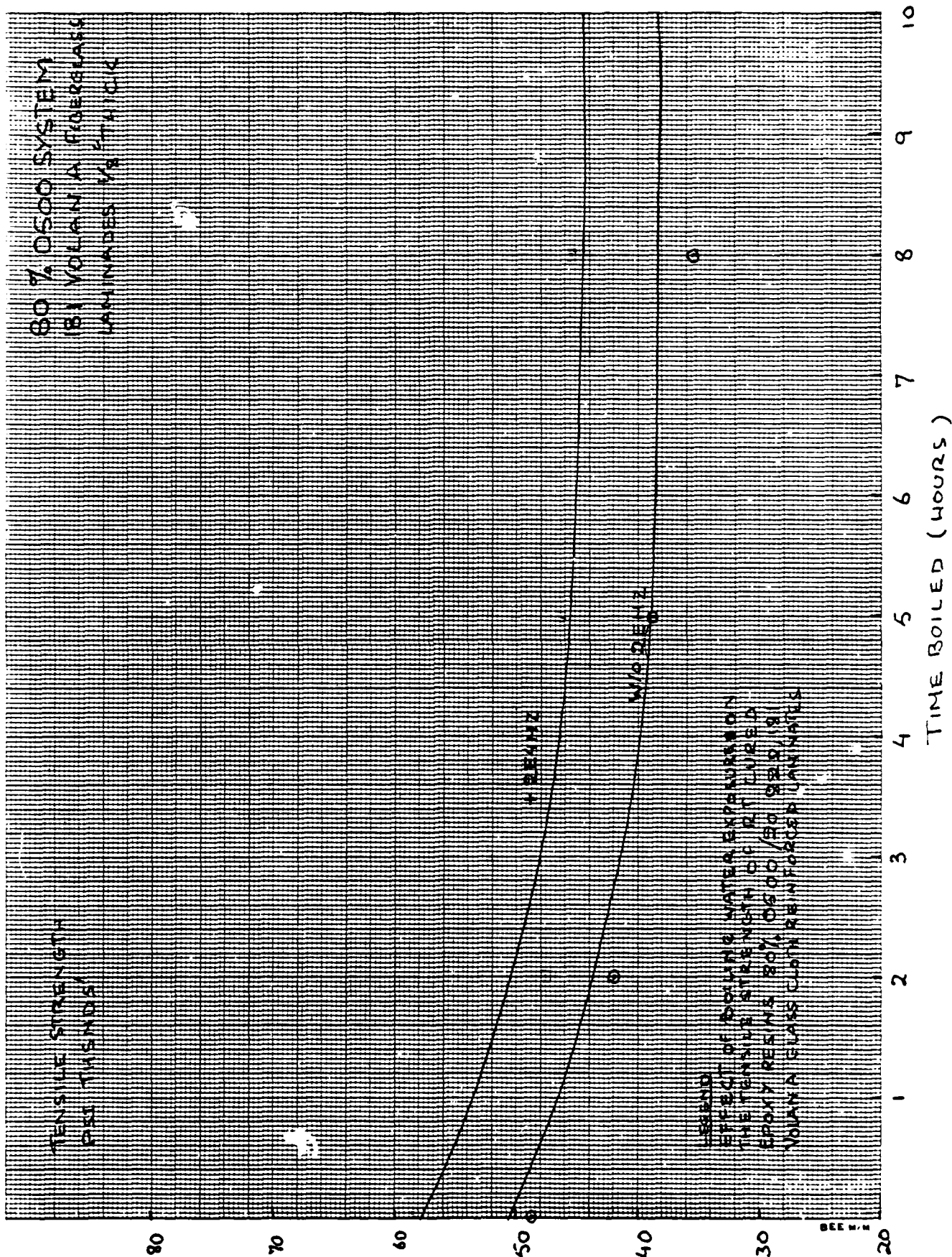


FIGURE 27

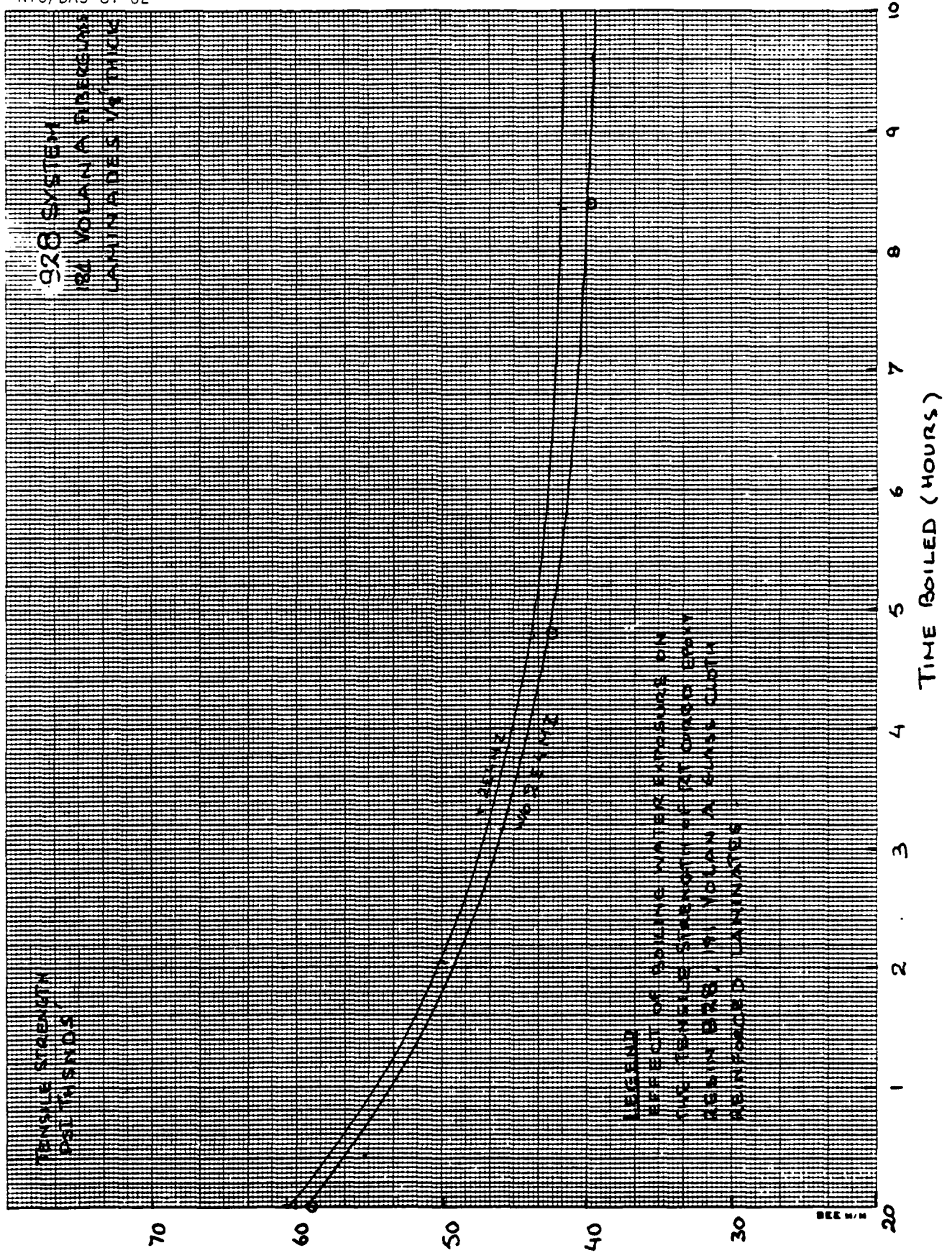


FIGURE 2'

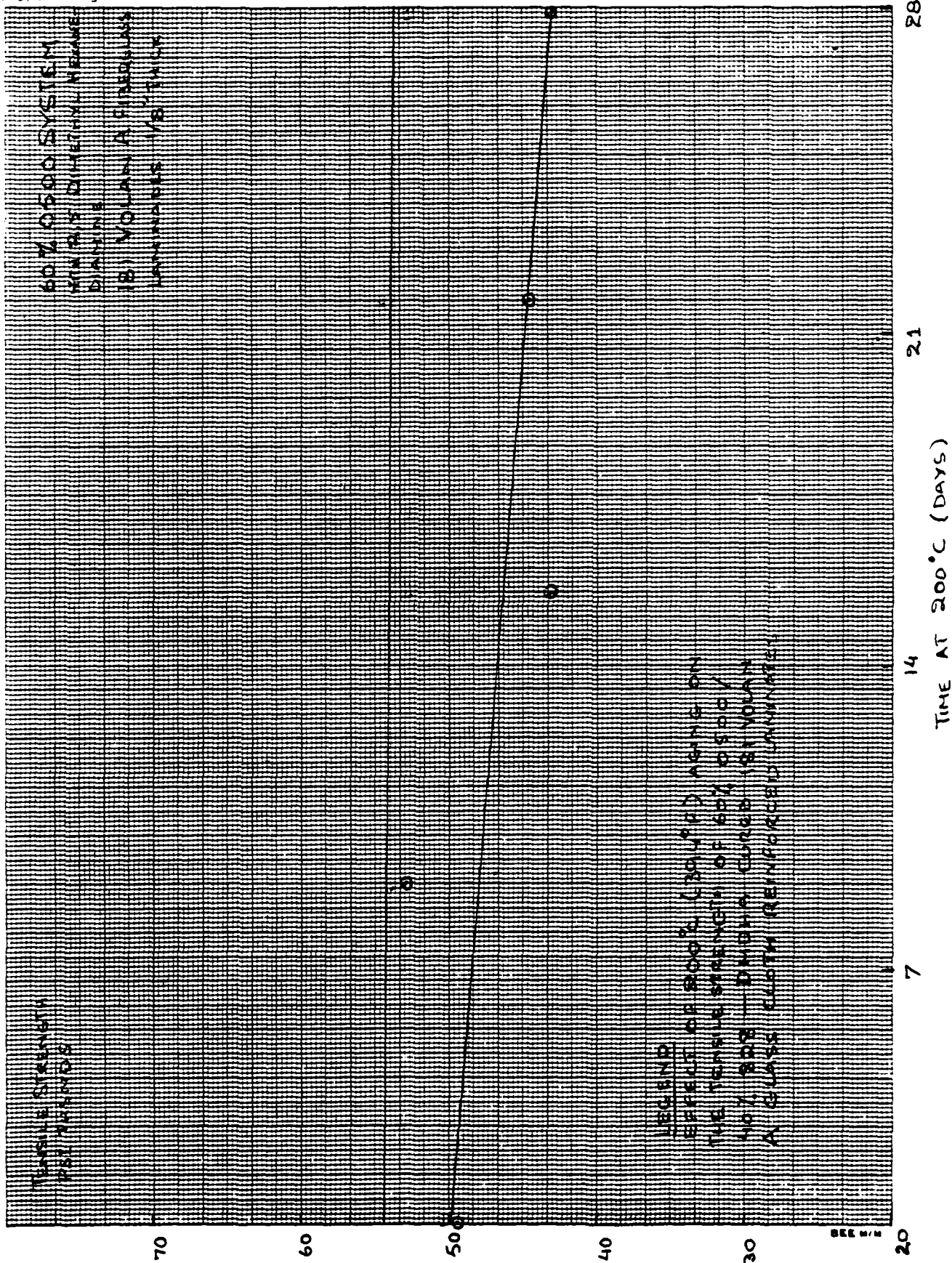


FIGURE 30

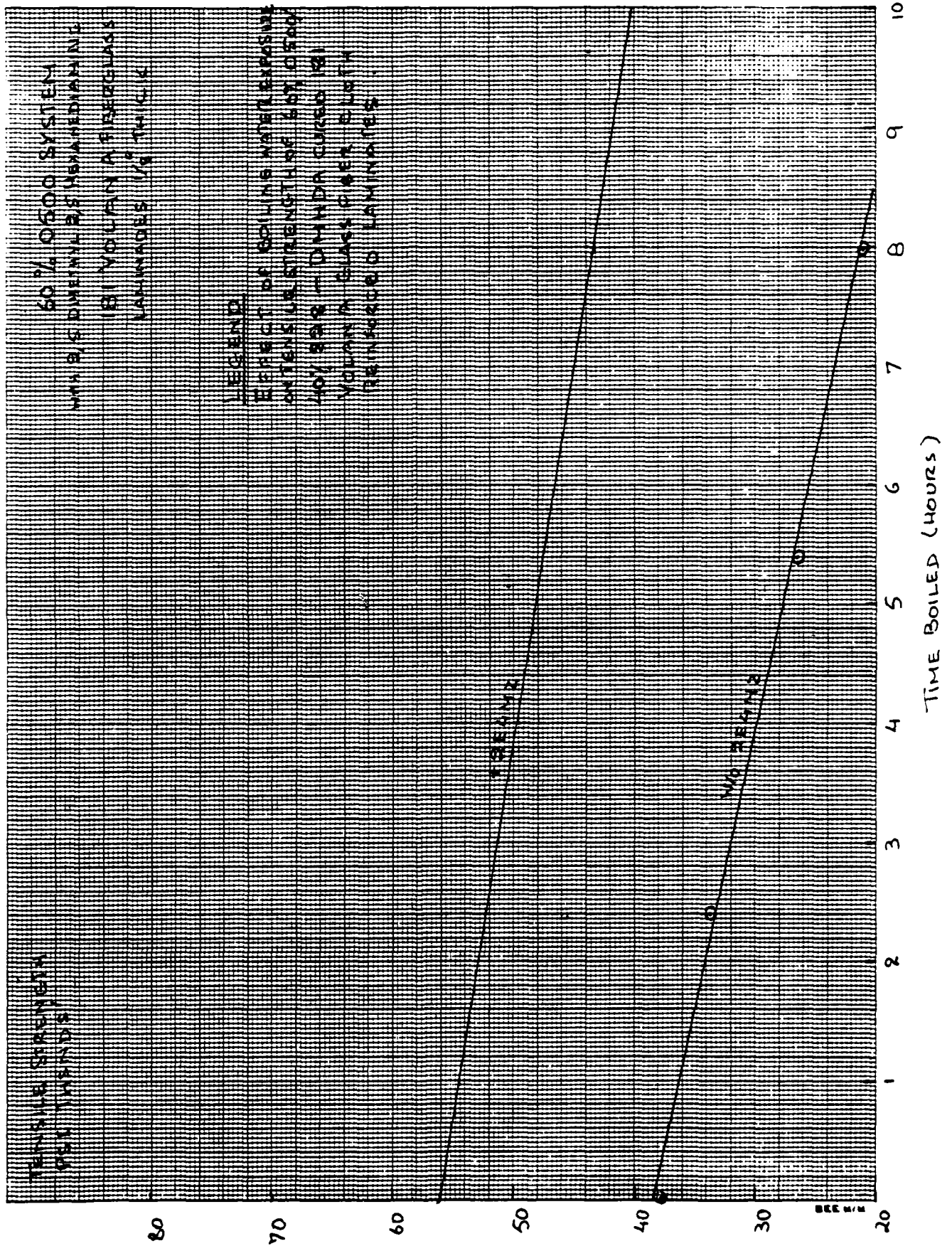


FIGURE 31

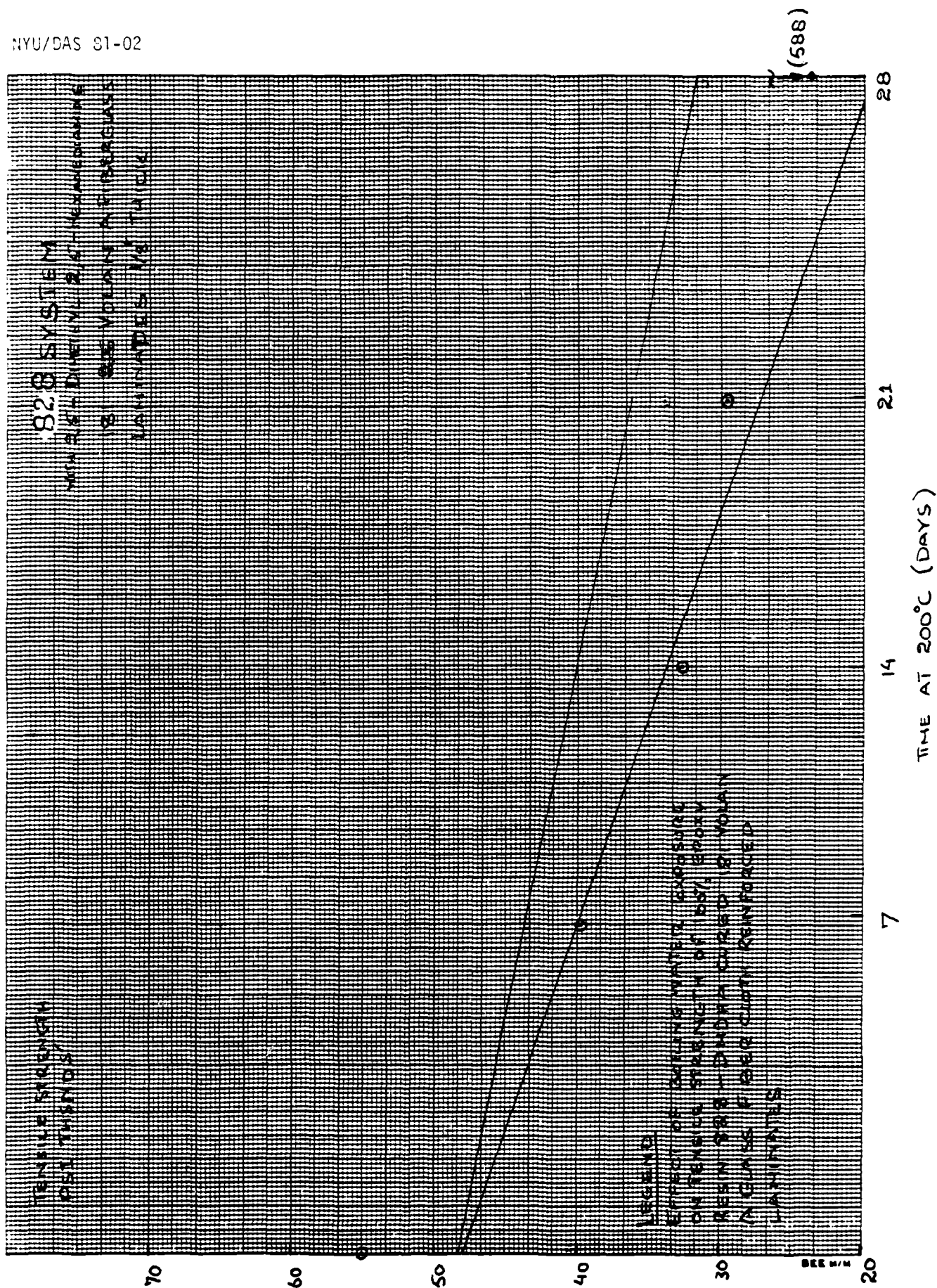
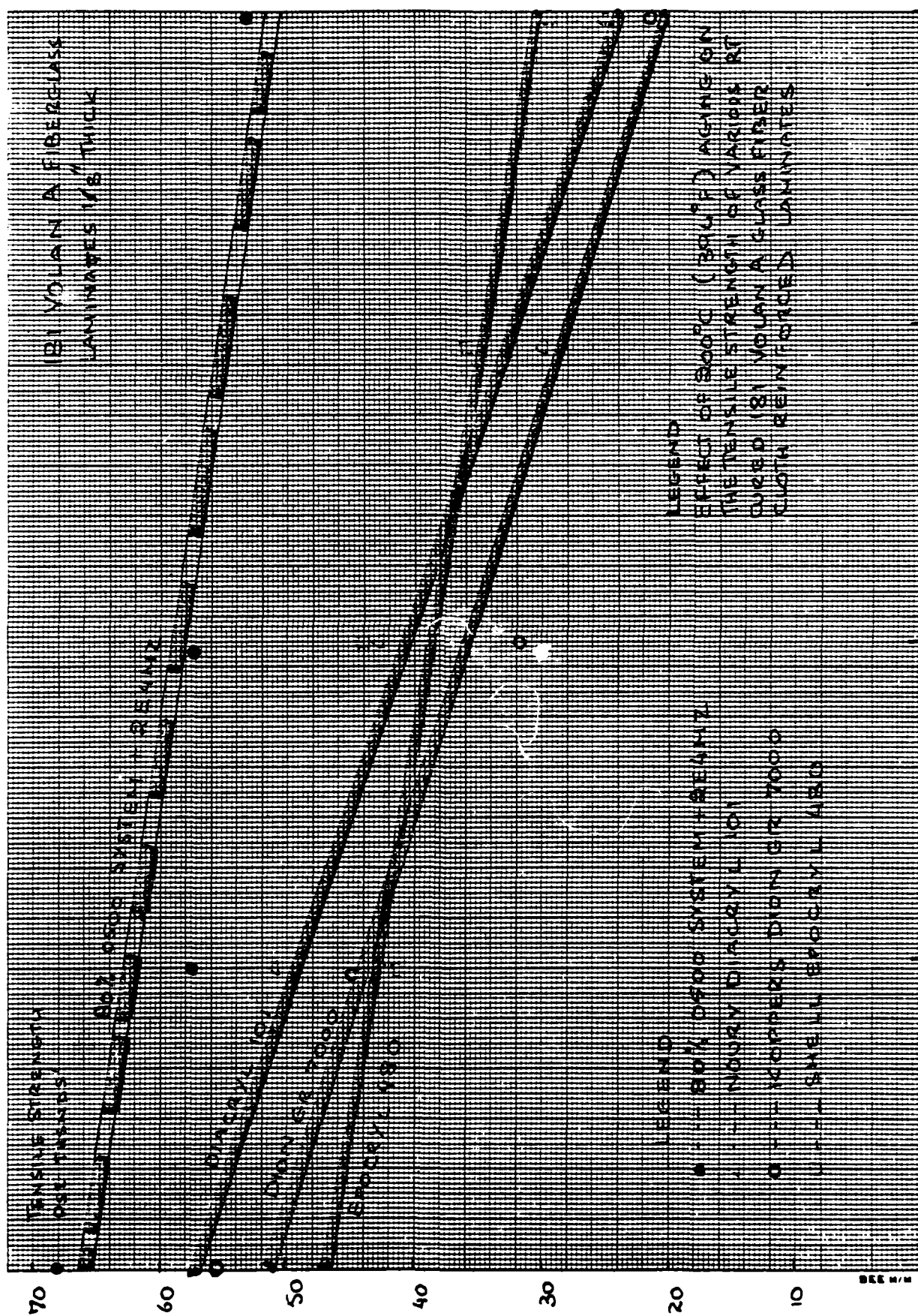


FIGURE 32



1B1 VOL 2 A FIBERGLASS
LAMINATES 1/8" THICK

ATMOSPHERIC

[illegible]

9
2
4
4
1

[illegible]

28

21

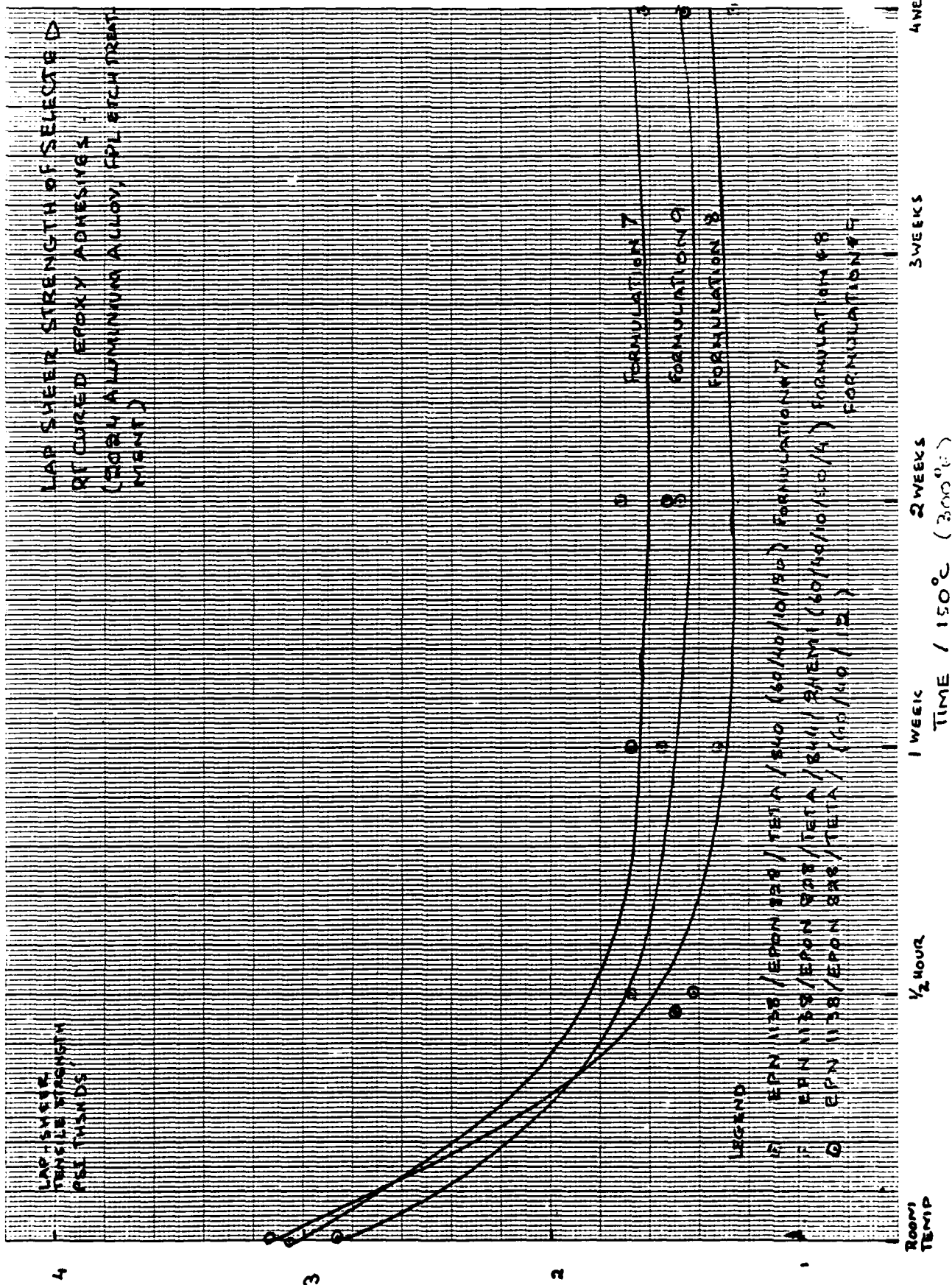
14

7

TIME AT 200°C (DAYS)

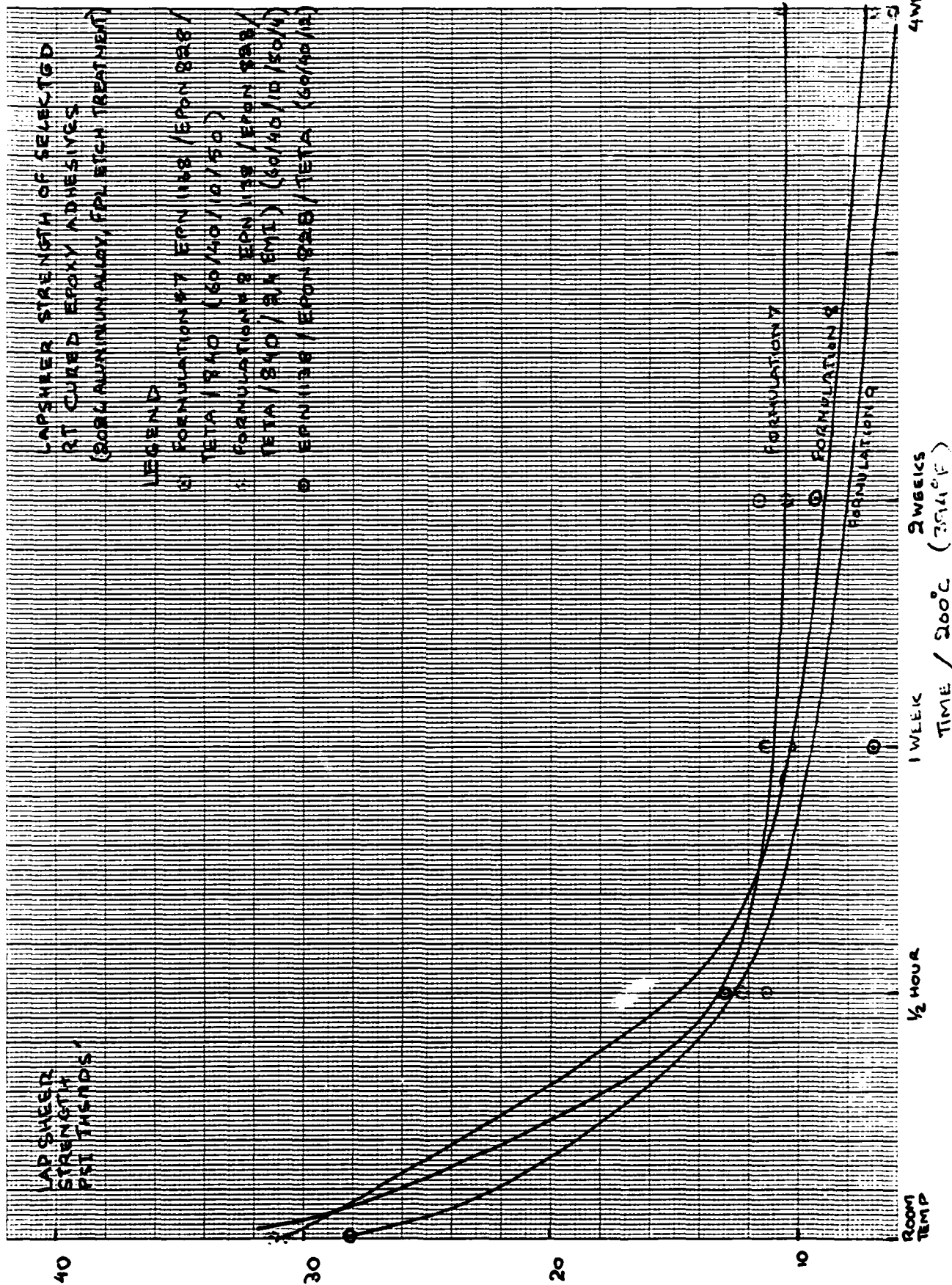
46 1517

FIGURE 34



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FIGURE 35



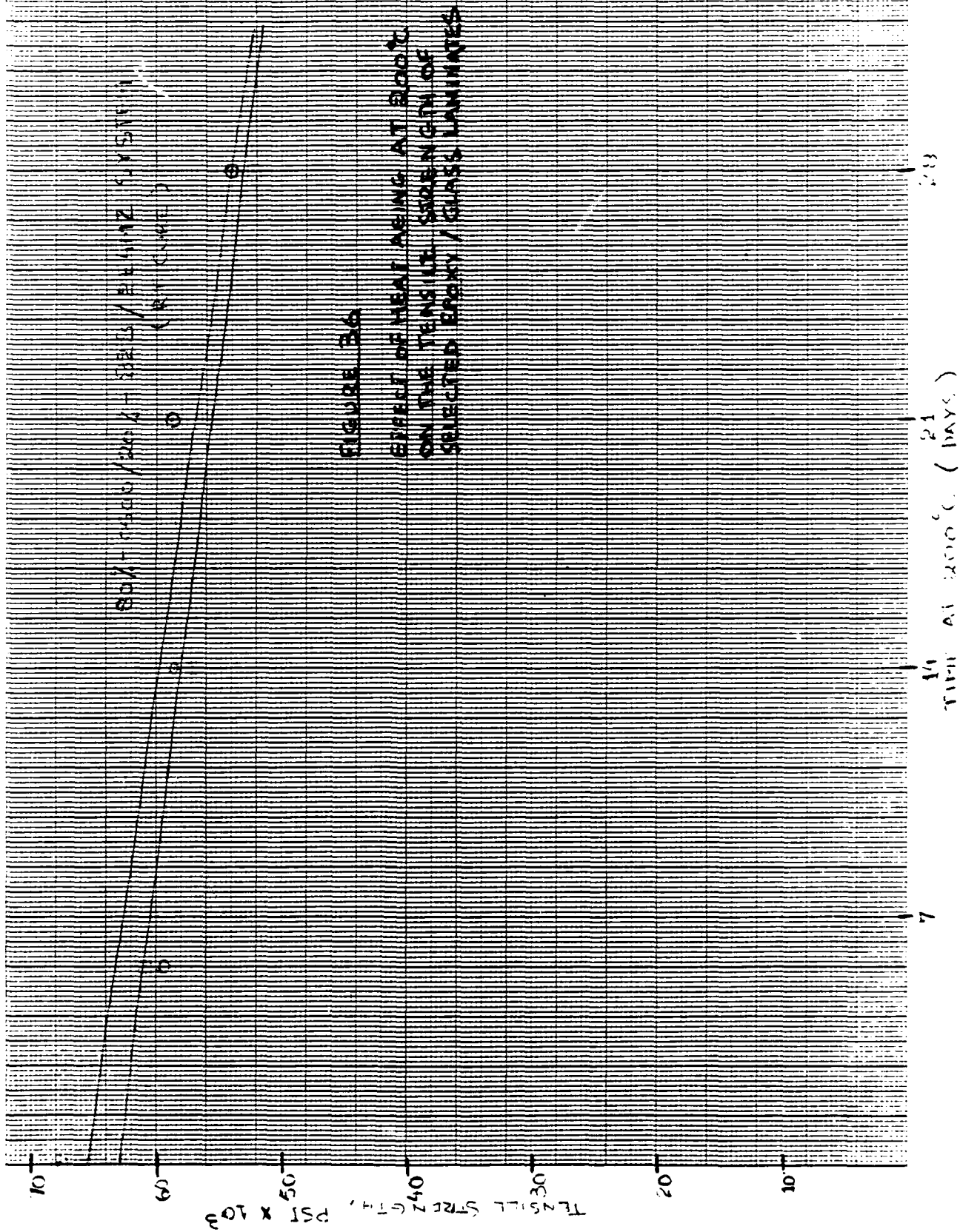


FIGURE 36

EFFECT OF HEAT AGING AT 200°C
ON THE TENSILE STRENGTH OF
SELECTED EPOXY / GLASS LAMINATES

